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Submitting Organization

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RESEARCH INST FOR SAFETY ENG

Document Title

STACK EMISSION - EMITTED TOLUENE DIISOCYANATE GAS TREATMENT
WITH ACTIVATED SLUDGE WITH ATTACHMENTS AND COVER LETTER
DATED 072287

Chemical Category

TOLUENE DIISOCYANATE (1321-38-6)

TELEX 383500   **{CONTAINS NO CBI**   CSL   (201) 263-7517

22 July 1987

86-8700000621

Document Processing Center (TS-790)
Office of Toxic Substances
Environmental Protection Agency
401 M Street, S.W.
Washington, D. C. 20460

Attention: 8(d) HEALTH and SAFETY REPORTING RULE (REPORTING)
             May 1, 1987

Dear   Madam:

As described at 40 C.F.R. 716.20(a) (10), the International Isocyanate
Institute (III) submits the enclosed studies on behalf of its members to
satisfy member reporting requirements under Section 8(d) of the Toxic
Substances Control Act. These studies are on chemicals added to the 8(d)
list on May 1, 1987. The studies are indexed by CAS numbers with chemical
name, III identification number and title provided.

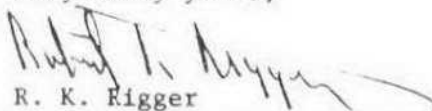Attachment #1 is an indexed list of completed studies.

Attachment #2 is a compilation of the reports from the completed studies.

Attachment #3 is an indexed list of studies that are currently in progress.

Please refer to the III identification number in any communication regard-
ing the report.

If the Agency needs further information, please do not hesitate to contact
me.

Very truly yours,

R. K. Rigger
Managing Director

RKR/c
enclosures

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8   Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10000	Prepolymeric MDI (Biphenylmethane Diisocyanat) with and without added Phenyl Isocyanate (PhI) - one hour acute inhalation toxicity.
10005	Determination of the concentration of vapor generated from monomeric 4.4'-Diphenylmethane Diisocyanate (MDI) by a dynamic method.
10008	Two-day study into the relation between polymeric MDI concentration values obtained by a QCM-Cascade, HPLC and Colorimetry.
10010	Liquid Waste after TDI/MDI decontamination.
10012	Literature Study on Reaction of Isocyanates with Biological Materials.
10013	Report on fire hazard of Isocyanate chemicals.
10014	Report on fire hazard of Isocyanate chemicals.
10018	Analytical methods to monitor aerosols of Polymeric 4,4'-Diphenylmethane-diisocyanate (MDI) at low concentrations.
10019	Aquatic life study phase II, step 2 Accumulation of TDI, MDI, TDA and MDA in fish and their toxicity.
10022	Generation and monitoring of breathable aerosols of polymeric 4,4'-diphenylmethane-diisocyanate (MDI).

INDEXED LIST OF COMPLETED STUDIES

CAS #101-68-8   Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
4,4'-Methylenebis(phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10026	Pre-polymeric diphenylmethane,4,4', diisocyanate (Petmar MDI) Pre-polymeric diphenylmethane,4,4', diisocyanate + phenyl isocyanate. 50 ppm. Pre-polymeric diphenylmethane,4,4', diisocyanate + phenyl isocyanate. 150 ppm. An experiment to investigate the relative sub-acute toxicity of the above substances in the rat by inhalation.
10050	Metabolism and toxicogenetics of Methylenedianiline.
10065	A study of the diffusion of MDI in rats contaminated via the respiratory system.
10074	Investigations on the microbial degradation of PU forams. Part II.
10075	Respiratory Sensitivity Study.
10076	Deposition of aerosol components on the hair of rats exposed to polymeric MDI aerosols.
10077	Acute inhalation toxicity study of polymeric MDI in rats.
10092	Biological action of TDI and MDI in water.
10129	Immunological aspects of Isocyanates.
10187	Isocyanates : Irritation and Hypersensitivity.
10188	Preliminary study on skin sensitization caused by MDI solutions.

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8   Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-p-phenylene diisocyanate
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MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE
10206	Aquatic life study Phase II, Step 2, Accumulation of TDI, MDI and their reaction products in Daphnia.
10223	TDI and MDI immunological studies. Summary report of research supported by the International Isocyanate Institute.
10234	Aquatic life study Phase II, Step 1. Biodegradation of TDI and MDI in the model river and marine water.
10243	Mortality among workers exposed to isocyanates. Feasibility Study.
10253	Sub-chronic (13 week) inhalation toxicity study of polymeric MDI aerosol in rats (part B2)
10258	Ecotoxicity of Toluenediisocyanate (TDI) Diphenylmethanediisocyanate (MDI) Toluenediamine (TDA) Diphenylmethanediamine (MDA)
10299	Aquatic Life Studies
10317	Production and control of breathable MDI aerosols for primal experiments.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 101-68-8   Benzene, 1,1'-methylenebis[4-isocyanato-
                        Methylenedi-p-phenylene diisocyanate
                        4,4'-Methylenebis(phenyl isocyanate)
                        MDI
                        4,4'-Diisocyanatodiphenylmethane

III NUMBER   TITLE

10360   Generation of 4,4' Diphenylmethane Diisocyanate (MDI) vapour

10386   Pharmacokinetics of MDI after inhalation exposure of rats to labelled MDI.

10391   Skin sensitization by isocyanates.

10393   Study of the burning characteristics of isocyanate chemicals.

10439   Di-Isocyanate Induced Asthma - Reactions to TDI, MDI, HDI and Hisamine.

24298   Acute Inhalation Toxicity (LC_{50}) in the Male Albino Rat.

INDEXED LIST OF COMPLETED STUDIES

CAS #1321-38-6   Benzene, diisocyanatomethyl-(unspecified isomer)

III NUMBER	TITLE
10010	Liquid waste after TDI/MDI decontamination.
10012	Literature Study on Reaction of Isocyanates with Biological Materials.
10013	Report on fire hazard of Isocyanate chemicals.
10014	Report on fire hazard of Isocyanate chemicals.
10019	Aquatic life study phase II, step 2 Accumulation of TDI, MDI, TDA and MDA in fish and their toxicity.
10024	Tolylene di-isocyanate three week inhalation toxicity in the rat.
10033	Stack Emission Part B : Emitted TDI Gas Treatment with Activated Carbon.
10034	Stack Emission Part A : Emitted TDI Gas Treatment with Activated Sludge.
10035	The toxicity and carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks.
10040	Reaction of TDI with water and with wet sand.
10044	Emission of Tolylene Diisocyanate (TDI) and Tolylene Diamine (TDA) in flexible polyurethane foam production lines.
10045	Emission of Tolylene Diisocyanate (TDI) and amines.
10055	Preparation and evaluation of a system for exposing rats Toluene Diisocyanate vapour.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER   TITLE

10057   Evaluation of a system for exposing hamsters to Toluene Diisocyanate vapour.

10064   A study of the diffusion rate of TDI in rats contaminated via the respiratory
               system.

10074   Investigations on the microbial degradation of PU foams. Part II

10075   Respiratory sensitivity study.

10089   Studies of Toluene Diisocyanate induced pulmonary disease.

10092   Biological action of TDI and MDI in water.

10094   Foam plant stack emission data.

10095   Stack Emission Part B : Emitted TDI Gas Treatment with Activated Carbon
               "Regeneration of Spent Activated Carbon".

10096   Stack Emission Part A : Emitted TDI Gas Treatment with Activated Sludge.

10098   Epidemiological study for effects of TDI.

10100   Histopathological observations on selected tissues of syrian hamsters exposed
               by inhalation to vapors of Toluene Diisocyanate (TDI) for 6 hours/day, 5 days/week
               for 4 weeks.

10116   Review of the incidence of rhinitis in rats exposed chronically to Toluene
               Diisocyanate vapour.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10117	Review of the national toxicology program carcinogenesis bioassay of Toluene Diisocyanate.
10121	Toluene Diisocyanate (TDI) proposed exposure standard.
10129	Immunological aspects of Isocyanates.
10142	Toluene Diisocysnate acute inhalation toxicity in the rat.
10153	A 30-day repeated inhalation toxicity study of Toluene Diisocyanate (TDI) in laboratory animals.
10159	The fate of Toluene Diisocyanate.
10162	Epidemiological study for effects of TDI.
10163	Validation of MCM 4000 personal monitor and MCM 4100 integrating reader/recorder system.
10168	Summary of work carried out on FE-A-14 III - 1 by H. Sakurai and co-workers.
10169	The toxicity and carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks.
10175	Emission of Tolylene Diisocyanate (TDI) and Tolylene Diamine (TDA) in flexible polyurethane foam production lines.
10184	Immunological studies on TDI exposed workers. Part I.
10187	Isocyanates : Irritation and Hypersensitivity.

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10206	Aquatic life study Phase II, Step 2, Accumulation of TDI, MDI and their reaction products in Daphnia.
10208	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Addendum Report. Vol. 2.
10210	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Vol. I
10223	TDI and MDI immunological studies. Summary report of research supported by the International Isocyanate Institute.
10233	The Toxicity and Carcinogenicity to rats of Toluene Diisocyanate vapour administered by inhalation for a period of 113 weeks. Addendum Report. Vol. 1
10234	Aquatic life study Phase II, Step 1. Biodegradation of TDI and MDI in the model river and marine water.
10237	Isocyanate monomer in PU foam.
10243	Mortality among workers exposed to isocyanates. Feasibility Study.
10258	Ecotoxicity of Toluenediisocyanate (TDI). Diphenylmethanediisocyanate (MDI) Toluenediamine (TDA). Diphenylmethanediamine (MDA)
10259	Sampling and Analysis of TDI atmospheres at Klinikum Grosshadern, Munich.

INDEXED LIST OF COMPLETED STUDIES

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE
10299	Aquatic Life Studies.
10307	Studies on the effects of TDI on living animals.
10308	Change of TDI in olive oil.
10321	Improvement in RAST for TDI. Parts A and B.
10340	Audit of the national toxicology program carcinogenesis bioassay of toluene diisocyanate.
10345	Isocyanate spillage control.
10348	Immunological Studies on TDI exposed workers Part II.
10349	Isocyanate hypersensitivity.
10382	The toxicity and carcinogenicity of Toluene Diisocyanate vapour when administered to mice over a period of approximately 2 years. Summary Report.
10383	The toxicity and carcinogenicity of Toluene Diisocyanate vapour when administered to mice over a period of approximately 2 years.
10391	Skin sensitization by isocyanates.
10393	Study of the burning characteristics of isocyanate chemicals.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS #1321-38-6   Benzene, diisocyanatomethyl-(unspecified isomer)

III NUMBER	TITLE
10416	Sampling and analysis of TDI atmospheres at Klinikum Grosshadern, Munich.
10430	Protective effect of drugs on late asthmatic reactions and increased airway responsiveness induced by Toluene Diisocyanate in sensitized subjects.
10433	The reactions of OH radicals with Toluene Diisocyanate, Toluenediamine, and Methylene Dianiline under simulated atmospheric conditions.
10434	Metabolism and disposition of ^{14}C-labeled Toluene Diisocyanate (TDI) following oral and inhalation exposure ; Preliminary studies.
10437	Toluene Diisocyanate-Induced Asthma: Bronchial Provocation and Reactivity Studies.
10438	Toluene Diisocyanate-Induced Asthma: Inhalation Challenge Tests and Bronchial Reactivity Studies.
10439	Di-Isocyanate Induced Asthma- Reactions to TDI, MDI, HDI and Histamine.

ATTACHMENT #1

INDEXED LIST OF COMPLETED STUDIES

CAS # 91-08-07   Benzene, 1,3-diisocyanato-2-methyl
                  TDI, 2-6-diisocyanate

III NUMBER   TITLE

24207   Disposition of 2,6-Toluene Diisocyanate in Fischer 344 rats

ATTACHMENT #2

COMPILATION OF REPORTS FROM III FILES
(AS INDEXED IN ATTACHMENT #1)

These reports are in envelopes labeled Attachment #2 and are packaged, along with an envelope,

addressed to:

                              Document Processing Center (TS-790)
                              Office of Toxic Substances
                              Environmental Protection Agency
                              401 M Street, S.W.
                              Washington, D. C. 20460

                              Attention: 8( ) HEALTH and SAFETY REPORTING RULE
                                         (ORTING) May 1, 1987

          from:

                              International Isocyanate Institute, Inc.
                              119 Cherry Hill Road
                              Parsippany, New Jersey 07054

containing a transmittal letter for these documents.

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 101-68-8   Benzene, 1,1'-methylenebis[4-isocyanato-
Methylenedi-n-phenylene diisocyanate
4,4'-Methylenebis (phenyl isocyanate)
MDI
4,4'-Diisocyanatodiphenylmethane

III NUMBER	TITLE

E-A-8

Study of chronic toxicity and carcinogenicity of polymeric MDI
aerosol in rats. Part C Study.

Current work authorized to begin June 1985.
To study chronic toxicity and carcinogenicity of polymeric
MDI aerosol in rats. Data sought - Effect on animal tissues.
Our current estimated completion date for this study is the
first quarter of 1989. It may be possible to complete this
study before 1989; however, it may require more time.
CIVO Institution, Tno., Toxicology and Nutrition, Utrechtsewe 848,
P.O. Box 306, 3700 A.J. Zeist, The Netherlands.

E-H-44

MDI sampling and analysis at CIVO

Current work authorized to begin November 1984.
To study consistency/comparability of various methods continuous/
discontinuous for determining the composition of atmospheres in
Study E-A-8 (Part C) above. Data sought - Analytical data on
polymeric MDI aerosol atmospheres.
Our current estimated completion date for this study is the first
quarter 1989. It may be possible to complete this study before
1989; however, it may require more time.
CIVO Institution, Tno., Toxicology and Nutrition, Utrechtsewe 848,
P.O. Box 306, 3700 A.J. Zeist, The Netherlands.

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER   TITLE

E-B-11   Epidemiological study of workers in U.K. flexible foam industries.

Current work authorized to begin Mid 1978.
To investigate whether working on flexible PU foam manufacturing
plants gives rise to increased expectation of decrements in lung
parameters above those due to ageing.
Data sought - monitoring of exposed workers' and controls' lung
parameters. Monitoring of airborne TDI (and on limited scale of
tertiary aliphatic amine) in the workplace.
Our current estimated completion date for this study is the
first quarter of 1989. It may be possible to complete this study
before 1989; however, it may require more time.
Tynestead Limited, Tynestead House, 22 Camberley Drive, Bamford,
Rochdale, Lancs, OL11 4 AZ, UK. and Medical Research Council,
20 Park Crescent, London, UK.

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER   TITLE

FE-AB-14   Epidemiological study of workers in Japan flexible foam industries.
                     Phase V.
                     _____

                     Current work authorized to begin August 1985.
                     To clarify relationship between TDI concentration and
                     chronological change in pulmonary and respiratory symptoms
                     of workers in PU foam plants. Data sought.
                     Monitoring of exposed workers' and controls' lung parameters.
                     Monitoring of airborne TDI in the workplace.
                     Our current estimated completion date for this study is the
                     first quarter of 1989. It may be possible to complete this
                     study before 1989; however, it may require more time.
                     School of Medicine, Keio University, Shinjuki-Ku, Tokyo, Japan.

ATTACHMENT # 3

INDEXED LIST OF STUDIES IN PROGRESS

CAS # 1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

E-E-22   Clean Stack Air Project

Current work authorized to begin March 1980.
To study ways in which TDI Emissions from flexible foam
plants can be removed from exhaust gases by carbon
absorption.
Data sought - Concentrations of TDI at inlets and outlets
of carbon absorption units.
Our current estimated completion date for this study is the
first quarter of 1989. It may be possible to complete this
study before 1989; however, it may require more time.
Dunlop (Now BTR, Silvertown House, Vincent Square, London, UK.

E-AB-40   An investigation into the mortality and cancer morbidity of
                              production workers in the UK flexible polyurethane foam industry.

Current work authorized to begin July 1987.
To compare the mortality and cancer morbidity experience of
production workers in UK flexible foam manufacturing plants with
those of unexposed controls and of the population at large, and to
determine, if appropriate, possible reasons for differing experiences.
Data sought.
Comparative Data on death and illness due to cancer, analysed statis-
tically. Data sought.
The expected date of termination of project is indeterminate since
it depends on results found at different intervals. The first
analysis will take place 1989.
Cancer Epidemiology Unit, University of Birmingham, Edgbaston,
Birmingham UK.

INDEXED LIST OF STUDIES IN PROGRESS

CAS #1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER   TITLE

NA-E-24   Fate of airborn TDI (Part II)

Current work authorized to begin May 1984.
To determine the fate of airborne TDI and the effects of moisture,
light, and atmospheric pollutants on TDI loss from the gas phase.
Our current estimated completion date for this study is the first
quarter of 1989. It may be possible to complete this study before
1989; however, it may require more time.
Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

NA-AB-26   Detecting delayed isocyanate sensitivity.

Current work authorized to begin May 1, 1987.
This research is being conducted to better detect delayed isocyanate
sensitivity in persons exposed and/or sensitized to isocyanates. In
1986, M. Karol's work was directed towards identification of
isocyanate-specific lymphocytes by class.
Our current estimated completion date for this study is the first
quarter of 1989. It may be possible to complete this study before
1989; however, it may require more time.
Dr. M. Karol, University of Pittsburgh, 130 Desoto Street,
Pittsburgh, Pennsylvania 15261

ATTACHMENT #3

INDEXED LIST OF STUDIES IN PROGRESS

CAS #1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER   TITLE

NA-AB-43   Improvement of RAST tests for TDI

                  Current work authorized to begin May 1, 1987.
                  This research is being conducted to improve RAST (Radiolabeled
                  Antibody Sorbent Technique) test for identifying exposure and
                  sensitization to TDI. Additional mechanistic work on TDI
                  sensitization is being conducted by Dr Brown. This includes
                  studying proteins in TDI exposed animals.
                  Our current estimated completion date for this study is the
                  first quarter of 1989. It may be possible to complete this study
                  before 1989; however, it may require more time.
                  Dr W. E. Brown, Carnegie-Mellon University, Pittsburgh, Pa. 15261.

NA-AB-50   TDI Reprotoxicity

                  The teratology study was initiated in the 4th quarter of 1986.
                  The reproduction study was initiated in the 2nd quarter of 1987.
                  This project evaluates both the "Developmental Toxicity of Inhaled
                  TDI in CD (Sprague-Dawley) Rats" and "Two-Generation Reproduction
                  Toxicity of TDI in CD (Sprague-Dawley) Rats."
                  Our current estimated completion date for this study is the first
                  quarter of 1989. It may be possible to complete this study before
                  1989; however, it may require more time.
                  Dr T. W. Tyl, Bushy Run Research Center, RD #4, Mellon Road, Export,
                  Pennsylvania 15632.

-5-

INTERNATIONAL ISOCYANATE INSTITUTE, INC.
119 CHERRY HILL ROAD
PARSIPPANY, NEW JERSEY 07054

TELEX 383600   {CONTAINS NO CBI}   (201) 263-7517

22 July 1987

86-870000

Document Processing Center (TS-790)
Office of Toxic Substances
Environmental Protection Agency
401 M Street, S.W.
Washington, D. C. 20460

Attention: 8(d) HEALTH and SAFETY REPORTING RULE (REPORTING)
             May 1, 1987

Dear Sir or Madam:

As described at 40 C.F.R. 716.20(a) (10), the International Isocyanate
Institute (III) submits the enclosed studies on behalf of its members to
satisfy member reporting requirements under Section 8(d) of the Toxic
Substances Control Act. These studies are on chemicals added to the 8(d)
list on May 1, 1987. The studies are indexed by CAS numbers with chemical
name, III identification number and title provided.

Attachment #1 is an indexed list of completed studies.

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Please refer to the III identification number in any communication regard-
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If the Agency needs further information, please do not hesitate to contact
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Very truly yours,

R. K. Rigger
Managing Director

RKR/c
enclosures

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(AS INDEXED IN ATTACHMENT #1)

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(REPORTING) May 1, 1987

from:

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INDEXED LIST OF STUDIES IN PROGRESS

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                   4,4'-Methylenebis (phenyl isocyanate)
                   MDI
                   4,4'-Diisocyanatodiphenylmethane

III NUMBER   TITLE

E-A-8   Study of chronic toxicity and carcinogenicity of polymeric MDI
                   aerosol in rats. Part C Study.

                   Current work authorized to begin June 1985.
                   To study chronic toxicity and carcinogenicity of polymeric
                   MDI aerosol in rats. Data sought - Effect on animal tissues.
                   Our current estimated completion date for this study is the
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                   P.O. Box 306, 3700 A.J. Zeist, The Netherlands.

E-H-44   MDI sampling and analysis at CIVO

                   Current work authorized to begin November 1984.
                   To study consistency/comparability of various methods continuous/
                   discontinuous for determining the composition of atmospheres in
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                   polymeric MDI aerosol atmospheres.
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INDEXED LIST OF STUDIES IN PROGRESS

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chronological change in pulmonary and respiratory symptoms
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School of Medicine, Keio University, Shinjuki-Ku, Tokyo, Japan.

ATTACHMENT # 3

INDEXED LIST OF STUDIES IN PROGRESS

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Data sought - Concentrations of TDI at inlets and outlets
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                                production workers in the UK flexible polyurethane foam industry.

Current work authorized to begin July 1987.
To compare the mortality and cancer morbidity experience of
production workers in UK flexible foam manufacturing plants with
those of unexposed controls and of the population at large, and to
determine, if appropriate, possible reasons for differing experiences.
Data sought.
Comparative Data on death and illness due to cancer, analysed statis-
tically. Data sought.
The expected date of termination of project is indeterminate since
it depends on results found at different intervals. The first
analysis will take place 1989.
Cancer Epidemiology Unit, University of Birmingham, Edgbaston,
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To determine the fate of airborne TDI and the effects of moisture,
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Battelle Columbus Laboratories, 505 King Avenue, Columbus, Ohio 43201

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Current work authorized to begin May 1, 1987.
This research is being conducted to better detect delayed isocyanate
sensitivity in persons exposed and/or sensitized to isocyanates. In
1986, M. Karol's work was directed towards identification of
isocyanate-specific lymphocytes by class.
Our current estimated completion date for this study is the first
quarter of 1989. It may be possible to complete this study before
1989; however, it may require more time.
Dr. M. Karol, University of Pittsburgh, 130 Desoto Street,
Pittsburgh, Pennsylvania 15261

INDEXED LIST OF STUDIES IN PROGRESS

CAS #1321-38-6   Benzene, diisocyanatomethyl- (unspecified isomer)

III NUMBER	TITLE

NA-AB-43   Improvement of RAST tests for TDI

Current work authorized to begin May 1, 1987.
This research is being conducted to improve RAST (Radiolabeled
Antibody Sorbent Technique) test for identifying exposure and
sensitization to TDI. Additional mechanistic work on TDI
sensitization is being conducted by Dr Brown. This includes
studying proteins in TDI exposed animals.
Our current estimated completion date for this study is the
first quarter of 1989. It may be possible to complete this study
before 1989; however, it may require more time.
Dr W. E. Brown, Carnegie-Mellon University, Pittsburgh, Pa. 15261.

NA-AB-50   TDI Reprotoxicity

The teratology study was initiated in the 4th quarter of 1986.
The reproduction study was initiated in the 2nd quarter of 1987.
This project evaluates both the "Developmental Toxicity of Inhaled
TDI in CD (Sprague-Dawley) Rats" and "Two-Generation Reproduction
Toxicity of TDI in CD (Sprague-Dawley) Rats."
Our current estimated completion date for this study is the first
quarter of 1989. It may be possible to complete this study before
1989; however, it may require more time.
Dr T. W. Tyl, Bushy Run Research Center, RD #4, Mellon Road, Export,
Pennsylvania 15632.

86-870000621

10034

FE - E - 15 /1 - A

Progress Report Number 1-A

to

The International Isocyanate Institute

by

Research Institute for Safety Engineering
5-6 Ginza 8-Chome,Chuo-ku,Tokyo,104,Japan

Title

Stack Emission,Part A

(Emitted TDI Gas Treatment with Activated Sludge)

Author

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Department of Safety Engineering
Yokohama National University

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0. Abstract

Tolylene diisocyanate and triethylene diamine would possibly be the pollutants for the environment if they are emitted. This report describes the possibility of treating the waste water containing triethylene diamine and the products after the hydrolysis of tolylene diisocyanate (TDI).

In Chapter 1, the general introduction to the water pollution was presented being associated with tolylene diisocianate and triethylene diamine.

At the same time, theoretical aspect and the chemistry of tolylene diisocyanate were given.

Chapter 2 described the acclimation of activated sludge which was used in the present experiments . The reader can obtain the precise informations from this chapter as regards the activated sludge if necessary.

In Chapter 3, the susceptibility of biological and chemical oxidations to the various materials was examined.

Corn steep liquor (synthetic substrate for the activated sludge) and glucose were easily oxidized both chemically and biologically. Aniline, hydrolyzed tolylene diisocyanate, and triethylene diamine were oxidized chemically but were slightly done biologically for a short period . The hydrolysis reaction of tolylene diisocyanate was proved to proceed almost completely. The COD of hydrolyzed tolylene diisocyate after the separation of solid suspension was very low.

The effect of aniline on the activated sludge was presented in Chapter 4 for the purpose of comparison with the successive chapters. Aniline did not give effect to the activated sludge cultured with domestic waste water as long as the dilution is appropriate. The treatment efficiency for aniline was mainly related to the biological phase. Chapter 5 suggested that the hydrolyzed TDI gave slight effect on the activated sludge under usual treatment condition. SVI and COD of the effluent were shown to be sensitive parameters for the treatment of waste containing TDI-water reaction products.

The biological effect on triethylene diamine was investicated in Chapter 6.

Triethylene diamine would be treated with activate sludge as long as the loading rate was low enough.

It was concluded as a whole that

(1) the hydrolyzed TDI and triethylene diamine gave slight effect on the activated sludge cultured with the domestic waste water,

(2) the acclimation of activated sludge with the water containing hydrolyzed TDI and triethylene diamine seemed to be possible.

1.   Introduction

1.1 Natural Purification of Waste Water

When a single, heavy charge of putrescible matter is poured
into a clean stream, the water becomes turbid, sunlight is
shut out of the depths, and green plants which by photo-
synthesis remove carbon dioxide from the water and release
oxygen to it, die off. Scavenging organisms increase in
number until they match the food supply. The intensity
of their life activities is mirrored in the intensity of
the biochemical oxygen demand (BOD). The oxygen resources
of the water are drawn upon heavily. In an overloaded
stream the supply of dissolved oxygen may become exhausted
Nitrogen, carbon, sulfur, phosphorus, and other important
nutritional elements run through their natural cycles, and
sequences of microbic populations break down (1) the waste
matters that have been added, (2) the natural polluting
substances within or entering the water, and (3) the food
made available by the destruction of green plants and other
organisms intolerant to pollution. The links of a food
chain are forged from available nutrients by the growth
and environmental adaptiveness of sequences of organisms.
The initial effect of pollution, on a stream, is to degrade
the physical quality of the water. As decomposition
becomes active, a shift to chemical degradation is

biologically induced. At the same time biological degrada-
tion becomes evident in terms of the number, variety, and
organization of the living things that persist or make
their appearance. In the course of time and flow the
energy values of a single charge of polluting substances
are used up. The biochemical oxygen demand is decreased,
and the rate of absorption of oxygen from the atmosphere,
which at first has lagged behind the rate of oxygen
utilization, falls into step with it and eventually outruns
it. The water becomes clear.

The natural purification of polluted waters is never fast,
and heavily polluted streams may traverse long distances
during many days of flow before a significant degree of
purification is accomplished.

1.2 Prameters of Pollutions

Degree of pollution and natural purification can be
measured physically, chemically, and biologically.
Measurements may be made of turbidity, color, odor,
nitrogen in its various forms, phosphorus, BOD, organic
matter, dissolved oxygen and other gases, mineral sub-
stances of many kinds, bacteria and other microorganisms,
and the composition of the larger aquatic flora and fauna.
Longitudinal changes in coliform concentrations establish
(1) the progress of bacterial self-purification, (2) the

relative hazard of infection incurred by ingesting the water, and (3) the degree of purification to which the water must be subjected before it can presumably be used with safety and satisfaction. When pollutional nuisance of receiving waters is the criterion, the DO and BOD, taken together, are relied upon to trace the profile of pollution and natural purification on which engineering calculations of permissible pollutional loadings can be based. The BOD identifies in a comprehensive manner the degradable load added to the receiving water or remaining in it at any time; the DO (dissolved oxygen) identifies the capacity of the body of water to assimilate the imposed load by itself or with the help of reaeration through oxygen absorbed mainly from the atmosphere, but possibly released to the water by green plants. Requisite standards of water quality will serve as guides to the tests that are meaningful in given circumstances; COD, for example, rather than BOD, may be the sentinel when acid wastes destroy saprophytes and other living things.

1.3 Aerobic Decomposition and the Meaning of BOD

Terrestrial organisms draw their oxygen from the atmosphere; aquatic organisms obtain theirs from the oxygen dissolved in water. Because water contains only about 0.8% oxygen by volume at normal temperatures (about $50^{\circ}F$),

whereas the atmosphere holds about 21% by volume, the aquatic environment is inherently and critically sensitive to the oxygen demands of the organisms that populate it. Determination of the amount of oxygen dissolved in water (DO) relative to its saturation value and of the amount and rate of oxygen utilization (BOD), therefore, furnishes a ready and useful means for identifying the pollutional status of water and, by indirection, also the amount of decomposable or organic matter contained in it at a given time. As shown in Fig. 1.1, the progressive exertion of the BOD of freshly polluted water generally breaks down into two stages: a first stage, in which it is largely the carbonaceous matter that is oxidized; and a second stage, in which nitrogenous substances are attacked in significant amounts and nitrification takes place. If the temperature of freshly polluted water is $20^{\circ}C$, for example, the first stage extends about to the 10th day. During this period the amount of BOD exerted in a unit of time relative to the BOD remaining to be exerted during the first stage is substantially constant. In the succeeding second stage the BOD rises sharply as nitrification becomes dominant. Oxygen is then put to use at a fairly uniform rate that is maintained for many days.

A knowledge of the progressive utilization of oxygen by

polluting substances is important for at least three reasons: (1) as a generalized measure of the amount of oxidizable matter contained in water, or the pollutional load placed on it, (2) as a means for predicting the progress of aerobic decomposition in polluted waters and the degree of self-purification accomplished in given intervals of time, and (3) as a yardstick of the removal of putrescible matter accompanying different treatment processes. However, only the first stage of decomposition appears to reproduce itself sufficiently well to be generalized in mathematical terms.

The first-stage BOD has generally been formulated as a first-order reaction. The concentration of oxidizable organic material present is the rate-determining factor, provided the oxygen concentration is greater than a critical value of about 4 mg per 1 at $20^{\circ}C$, for example. Because the reactions involved are enzymatic, the first-order equation may be written for the lack of oxygen dependence.

$$y = L\left[1 - \exp(-kt)\right] = L(1 - 10^{-k't}),$$

in which L is the initial or first-stage BOD of the water, y is the oxygen demand exerted in time t, and k or k' are the rate constants related respectively to base e and base 10. The BOD remaining at time t equals (L - y), and the

proportion of BOD exerted in time t is $y/L = 1 - \exp(-kt)$ $= (1 - 10^{-k't})$, k' equaling 0.4343k.

1.4 Biological Treatment

As presently conceived and practiced, the biological treatment of waste waters is not a single operation but a combination of interrelated operations that may differ in spatial distribution, proceed at different rates in time, and be accomplished by biomasses that are unlike in structure.

First in time and importance is the transfer of impurities from the waste waters to film, floc, or other forms of biomasses by interfacial contact and associated adsorptions and absorptions. This operation is fast and effective if the interface between the liquid and the biomass is large, if the concentration gradient of the substances to be removed from one phase to the other is steep, and if obstructive liquid films and concentrations of interfering substances do not build up on the interface. Quality as well as extent of contact is therefore important.

Second in time and equally significant is the preservation of this quality of contact. It is accomplished primarily by the oxidation of organic matter and synthesis of new cells. Contact quality is preserved because of the tendency of dissolved matter to change in concentration in such

fashion as to decrease the surface tension in the biotic film or floc. Substances concentrating at surfaces are adsorbed; adsorbed substances are decomposed by the accumulating enzymes of living cells; new cells are synthesized; and end products of decomposition are washed into the waters or escape to the atmosphere. Examples are (1) the transfer of salts, such as nitrates, back to the wastewater because they increase the surface tension of the interface, and (2) the escape of gases, such as CO_2, because of their lower partial pressure in the contiguous atmosphere. Conversion of the biomass into settleable or otherwise removable solids is a vital matter. This third operation proceeds in synchrony with the preservation of the quality of contact and determines the over-all effectiveness of the process.

The progress of biological purification is illustrated in Fig. 1-2. Interfacial transfer or adsorption is the rate-determining step. It can hold its lead, because slow operations - such as the preservation of contact quality and the settleability and stabilization of the biomass - are in the nature of things shifted out of the time stream of happenings in the liquid phase to proceed at a more leisurely pace in the solid phase of the biomass. Biological treatment shares this effect with the biological

self-purification of receiving waters, in which suspended
solids are laid down on the stream bottom to decompose
slowly in the benthal environment.

If decomposition is designed to approach full stabilization
of waste flocs or sloughed films within the principal
treatment unit itself, a fourth operation is added to
over-all treatment demands.

The most advanced biological treatment systems are normally
preceded by primary settling tanks. The biological or
secondary component is then composed of the biological
unit proper, normally with its own secondary settling tank.
However, as illustrated in Fig. 1-3, some partial or
complete recirculating systems dispatch their solids to
the primary tank.

Recirculation of waste water flows through biological
treatment units distributes the load of impurities imposed
on the units and smooths out the applied flow rates. In
this way normal as well as shock loadings can be affected
favorably.

1.5 Activated Sludge Systems (ASS)

1.5.1 Microbiological system

    (A) Biological Degradation of Waste Water

        Waste water which contains various organic compounds
        is subject to the coaguration into biomass and/or

the biological degradation when they contact activated sludges. The soluble organic compounds are decomposed into H_2O and CO_2 via. the adsorption onto and accumulation into the activated sludges.

The biological degradation of waste water is affected by its quality because the reactivity of the activated sludge is sensitively dependent on the structure of the organic compounds.

The biological oxidation proceeds through the following four phases:

(1) The adsorption of organic compounds onto the activated sludge

(2) Accumulation of organic compounds into the activated sludge

(3) Consumption due to the growth and self-sustaining of the activated sludges.

(4) Endogenous respiration

The above processes can be expressed as

$$CxHyOz + O_2 \xrightarrow{enzyme} CO_2 + H_2O - \Delta H \quad \dots \quad (1)$$

(Oxidation of waste water)

$$CxHyOz + NH_3 + O_2 \xrightarrow{enzyme} \text{cell material} +$$
$$CO_2 + H_2O - \Delta H \quad \dots\dots\dots\dots\dots\dots\dots \quad (2)$$

(Synthesis of cell material)

$$\text{Cell material} + O_2 \xrightarrow{enzyme} CO_2 + H_2O +$$
$$NH_3 - \Delta H \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (3)$$

(Endogenous respiration)
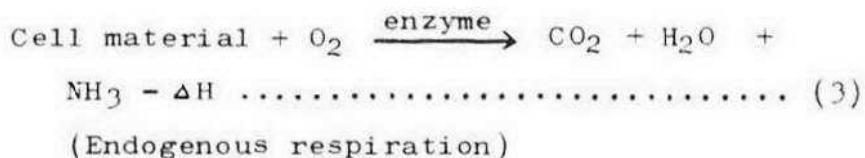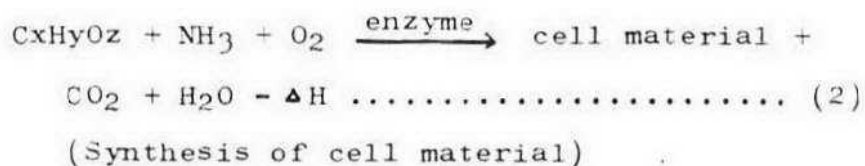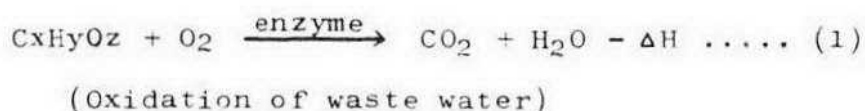
where H is the enthalpy change associated with the reaction. In other words, $-\Delta H$ is the heat of reaction. The nitrogen and sulfur compounds are oxidized into sulfates and nitrates.

(B) <u>Growth of activated sludge</u>

One of the most important processes of activated sludge systems is the growth of the microorganisms. Theoretical treatment of its growth has not necessarily been sufficiently developed for the flow culture systems, while it was done for the batch culture.

The growth phase of the batch culture in the vessel such as Fig. 1.4 will be given in brief.

The typical growth of biomass with time can be represented as shown in Fig. 1.5.

(a) Induction phase

In this peri$\cdot$d, the cell prepares for the fission until the enough substrates are accumulated in the biomass.

(b) Logarithmic growth phase

In this period, the cell concentration X (mg. cell/L) increases according to the following relation.

$$\frac{dX}{dt} = Y_{x/s} \left(- \frac{dS}{dt} \right) \quad \dots\dots\dots\dots\dots\dots\dots \quad (4)$$

where S (mol/l) and $Y_{x/s}$ (mg. cell/mol) are the concentration of substrate and yield coefficient of the biomass for a unit substrate respectively. Being analogous to the Michaelis-Menten's equation, the removal rate of substrates is expressed by

$$\nu = \nu_m \frac{S}{K_s + S} \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (5)$$

where

ν (mol/mg. cell-hr):   Specific substrate removal rate.

$$(= - \frac{1}{X} \frac{dS}{dt})$$

S   (mol/l):   the substrate concentration

K_s (mol/l):   the saturation constant

Since

$$Y_{x/s} \; \nu_m = \mu_m$$

the combination of Eq. (4) with Eq. (5) produces the following relation.

$$\frac{dX}{dt} = X \nu_m \, Y_{x/s} \frac{S}{Ks + S}$$

$$= \mu_m \; \frac{S}{K_s + S} X \quad \dots\dots\dots\dots\dots\dots\dots\dots \quad (6)$$

In the logarithmic growth phase, the assumption S >> Ks holds. Thus, Eq. (6) is expressed as

$$\frac{dX}{dt} = \mu_m X$$

and gives the following solution of X.

$$X = Xo \exp (\mu_m t) \dots\dots\dots\dots\dots\dots (7)$$

m is referred to specific growth rate with the dimension of (hr^{-1}).

(c) and (d) Transition and static phases.

The activated sludge terminates growth after a transition period when the following conditions are given

(i) the shortage of substrates and nutrients

(ii) the shortage of oxygen supply

(iii) the accumulation of toxic matters

(iv) the shortage of growth factor such as vitamins

(e) Decay phase

After the activated sludge stays at the static phase for a period, it starts to decompose following Eq. 8.

$$\frac{dX}{dt} = X - K_d X = m \frac{S}{K_s + S} X - K_d X \dots\dots (8)$$

where kd is the decomposition constant (hr^{-1}).

(C) The rate of oxygen consumption

The aerobic oxidation of organic material is conducted by the respiration of microorganism.   The aerobic

oxygen balance is given according to the relation

$$A(-\Delta S) = B(\Delta X) + \Delta O_2 \quad \cdots\cdots\cdots\cdots\cdots (9)$$

where   X;   the concentration of microorganism

$(mg/1)$

A;   the oxygen demand for the complete

oxidation of organic matter

$(mgO_2/mg:$ organic matter)

B;   the oxygen demand for the complete

oxidation of activated sludge

$(mgO_2/mg$ MLSS)

At the same time, Eq (10) holds for the aerobic

consumption of O_2.

$$\Delta O_2 = moX \Delta t + \frac{1}{Y_{go}} \Delta X \quad \cdots\cdots\cdots\cdots\cdots\cdots (10)$$

where   mo;   maintenance constant for oxygen

$(mgO_2/mg$ MLSS. hr)

Y_{go};   yield coefficient for oxygen

The combination of Eq (9) and (10) gives

$$\frac{dO2}{dt} = \left(\frac{A}{1 + BY_{go}}\right)\left(\frac{-dS}{dt}\right) + \left(\frac{B \cdot Y_{go} \, m_o}{1 + BY_{go}}\right)X \quad \cdots\cdots (11)$$

Here, the specific substrate removal rate for the
unit hydraulic retention time in an aeration tank
can be expressed as

$$\frac{1}{X}\left(-\frac{ds}{dt}\right) = \left(\frac{So - S}{X}\right) \cdot \frac{F}{V} \quad \dots\dots\dots\dots\dots\dots (12)$$

F; influent of waste water (m^3/day)

V; volume of tank (m^3)

(V/F) ; hydraulic detention time

So; concentration of substrate of influent

Elimination of (-ds/dt) from Eq. 11 and Eq. 12 gives

$$V\frac{d[O_2]}{dt} = aF(So - S) + bVX \quad \dots\dots\dots\dots\dots\dots (13)$$

where $a = A/(1 + BY_{go})$;   Oxygen consumed for the oxidation and growth of micro-organism.

$b = moBY_{go}/(1 + BY_{go})$;   specific oxygen consumption rate required for the maintenance metabolism.

$(mgO_2/mg$ MLSS $- hr)$

1.5.2   Activated Sludge Processes

In the activated sludge processes the waste water is oxydized and stabilized through the complicated biological reactions.

It is almost impossible to elucidate the whole processes which occur in an activated sludge system.

However, it can controled practically by using the following parameters.

(i) quality of the waste water

(ii) loading rate

(iii) type of reactor

(iv) growth of activated sludge

(v) transport of oxygen

(vi) settling character of the sludge

To find out the relations among these parameters, the mathematical model is given below. The meaning of the parameters will become clear.

(A) <u>Growth and removal of substrates</u>

As is given in the preceding chapter, the relation between the rowth of biomass and the removal of substrate can be expressed by

$$\frac{dX}{dt} = Y(\frac{dS}{dt}) - k_d X \dots\dots\dots\dots\dots\dots\dots (14)$$

where

$\frac{1}{X}(\frac{dX}{dt})$; net specific growth rate

Y; yield coefficient

$\frac{dS}{dt}$; substrate removal rate

kd; decomposition constant

X; microorganism concentration

From Michaelis – Menten's equation for the enzyme reaction, the following relation is obtained.

$$\frac{dS}{dt} = \mathcal{V}_m \frac{S}{Ks + S} \quad \dots \dots \dots \dots \dots \dots \dots \dots (15)$$

$\mathcal{V}_m$; maximum specific removal rate of a substrate

S: actual substrate concentration

Ks; substrate concentration at the half of the

max. substrate removal rate

by dividing Eq. 14 by X, Eq. 16 is deduced.

$$\frac{1}{X} \left(\frac{dX}{dt}\right) = Y \frac{1}{X} \left(\frac{dS}{dt}\right) - Kd \quad \dots \dots \dots \dots \dots \dots (16)$$

The combination of Eq. 15 and Eq. 16 conducts Eq. 17

$$= Y \frac{\mathcal{V}_m S}{Ks + S} - Kd \quad \dots \dots \dots \dots \dots \dots \dots (17)$$

For the definite change, Eq. 16 can be approximated

by

$$\frac{1}{Xm} \left(\frac{\Delta X}{\Delta t}\right)_m = Y \frac{1}{Xm} \left(\frac{\Delta S}{\Delta t}\right) - Kd \quad \dots \dots \dots \dots (18)$$

where the sufix m represents the constancy of biomass

and substrate.

Here, $Xm/(\Delta X/\Delta t)m$ is referred to mean cell residence

time or biological solid retention time.

That is, $Oc = Xm/(\Delta X/\Delta t) \cdot m \quad \dots \dots \dots \dots \dots (19)$

In Eq. 19, Xm is equal to the total amount of activated

sludge and $(\Delta X/\Delta t)$ is to the rate of the biomass

removal from the aeration tank. Using the relations

$$U = (\Delta F/\Delta t)_m /X_m \quad \dots \dots \dots \dots \dots \dots \dots (20)$$

$$= O_c^{-1} = YU - K_d \quad \dots \dots \dots \dots \dots \dots \dots (21)$$

the percentage of the substrate removal from the
activated sludge system is given by

$$E = \frac{Si - Se}{Si} \times 100 \ (\%) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (22)$$

where sufix i and e represent the influent and effluent,
respectively.

In order to obtain the concentration of substrates
Eq. 21 is rewritten with Eq. 15 and Eq. 20 into Eq. 23

$$Se = Ks(1 + Kd\theta c)\theta c(YK - Kd) - 1 \quad \ldots\ldots\ldots\ldots\ (23)$$

From Eq. 17 and Eq. 21

$$U = kSe/(Ks + Se) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (24)$$

$$Se = UKa/(K - U) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (25)$$

Therefore, substrate concentration in the effluent is
a function of θc or U.

Finally, Se can be estimated from Y, K and K_d .

(B) The interpretation of the parameters

    (a) Mixed liquor suspended solid (MLSS) and mixed
liquor volatile suspended solid (MLVSS)

        In the activated sludge processes it is almost
impossible to separate the suspended solids into
simple components. In order to evaluate the
quantity of the suspended solid, the cake removed
from the mixed liquor by filtration is measured.
The dried cake thus obtained from the liquor

mixture of one liter is referred to MLSS(mg/l or ppm).
On the other hand, MLVSS means the organic compound
included in the cake. MLVSS is obtained by measur-
ing the heat generated by the combustion of the
cake.

MLVSS is important for the waste water containing
large amount of inorganics.

(b) Concentration of organic matter

The microorganisms consume oxygen to oxidize the
soluble organic matter. Thus, the amount of oxygen
consumed by the microorganisms could be an index
of the concentration of organic matter. This
quantity is called biological oxygen demand (BOD).
On the other hand, chemical oxygen demand (COD)
means the oxygen consumption due to the chemical
oxidation of organic matter.

(c) Sludge volume index (SVI)

This indicate the settling character of the acti-
vated sludge. The settling character is important
for the separation of sludge from the liquid-solid
mixture.

The actual index is given as

$$SVI = \frac{SV_{30}}{MLSS} \times 10^4$$

where SV_{30} means the ratio of water layer to cake
layer when the solid-liquid mixture is kept in 1
graduated cylinder.

SV_{30} is expressed with percentage of cake layer to
the total mixture when it is kept in a static state
for 30 minutes.

(d) F/M ratio

F/M ratio is defined by the following equation

$$F/M = \frac{CODin \times Q}{MLSS \times v}$$

where

        CODin;   influent COD (ppm)

           Q;   volume of influent waste water

               (L /day)

           V;   volume of tne aeration tank

               (L)

        MLSS;   mixed liquor suspended solid

               (mg/L or ppm)

The treatment efficency increases with the resident time
of wast water in the aeration tank and with the
amount of the activated sludge.

Thus, the ratio of the amount of substrate in the
influent to that of activated sludge is an im-
portant factor.

In the present operation F/M remains less than 0.2.

(e) Oxidation - reduction potential (ORP)

The electrode potential of inert electrode such as platinum in the mixed liquor is dependent upon the condition of activated sludge. However, the interpretation for ORP is not fully developed so far. Usually, the activated sludge in a good condition shows the potential of +100 to +550 mv against the standard hydrogen electrode. The decrease in oxygen concentration and increase in loading of substrates shifts the potential to the negative value.

(f) Hydrogen ion concentration (pH)

The usual pH value for biological ecosystem is between 6.8 and 7.4. When the activated sludge is overaerated, pH decreases to about 6.0 and the dispersion of sludge floc occures.

The increase in pH to about 7.5 induces the poor settling of the activated sludge

(g) Dissolved oxygen (D.O.)

The dissolved oxygen in the aeration tank should be maintained between 0.5 to 2 ppm in order to keep the conditions of activated sludge.

1.6 Glossary as for Activated Sludge Systems

1) Endogenous Respiration

The shortage of the substrate causes the selfdecomposition of the microorganisms to produce energy to sustain their life. This is called endogenous respiration.

2) Cell material

The chemical composition of the cell material in the usual conditions can be expressed as $C_5H_7NO_2$. When a cell accumulates the substrates, its composition would be $C_5H_7NO_2 \cdot C_xH_yO_z$, which is dependent upon the character of waste water.

3) Yield coefficient: Y_{go}

This means the growth of microorganisms when the unit amount of oxygen is consumed.

4) Michaelis-Menten's equation

Suppose that substrate, S, react with enzyme, E, to produce the complex ES and ES decomposes into product P and E. That is

$$E + S \underset{K_{-1}}{\overset{K_{+1}}{\rightleftharpoons}} ES \xrightarrow{K_{+2}} E + P$$

The yielding rate of product is given by

$$V = \frac{V_m \, S}{K_m + S}$$

where

$$Vm = K_{+1} [E]_o$$

$$Km = \frac{K_{-1} + K_{+2}}{K_{+1}}$$

The above equation is referred to Michaelis-Menten's equation.

5) Maintenance constant

The microorganisms require two kinds of energy, that is, the energy to grow and that to maintain their life. The oxidation processes of substrate to produce the latter energy is referred to maintenance metabolism. The amount of this energy for the unit quantity of microorganisms is called maintenance constant.

6) Mean cell residence time (biological solid retention time): θc

The microorganism is very active when cell fissions take place.

Thus, the activity of microorganism in the activated sludge system is higher as their residence time is shorter. The parameter θc would correspond to the activity of activated sludge.

In the other hand, the activated sludge with small θc could be affected much sensitively for the loading conditions. Therefor, the control of the activated sludge processes is not easy in this case.

1.7 Chemistry of Tolylene Diisocyanate (TDI)

Diisocyanate toluene or tolylene diisocyanate (TDI) has such structure as Fig. 1.6. TDI is very reactive and react with various kinds of compound.

Especially, TDI is highly reactive to the compounds having active hydrogen atoms. The reaction can be expressed as

$$R \cdot NCO + HX \longrightarrow R \cdot NH \cdot CO \cdot X$$

The reactivity of the active hydrogen atoms is in the following order.

$$A \quad k \cdot NH_2 > Ar \cdot NH_2 > H_2O \doteqdot R \cdot CH_2OH > R^1R^2CHOH \doteqdot$$

$$R^1R^2R^3C-CH > \text{active } CH_2 > Ar \cdot OH > R \cdot COOH > R \cdot CO \cdot NH_2$$
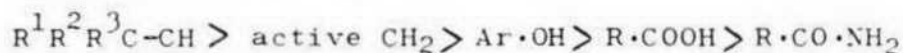
This indicates that TDI reacts with water to a great extent. The hydrolysis of TDI yields CO_2 and amine finally.

$$R \diagdown \begin{matrix} NCO \\ NCO \end{matrix} + 2H_2O \longrightarrow R \diagdown \begin{matrix} NH \cdot COOH \\ NH \cdot COOH \end{matrix}$$

$$\longrightarrow R \diagdown \begin{matrix} NH_2 \\ NH_2 \end{matrix} + 2CO_2$$
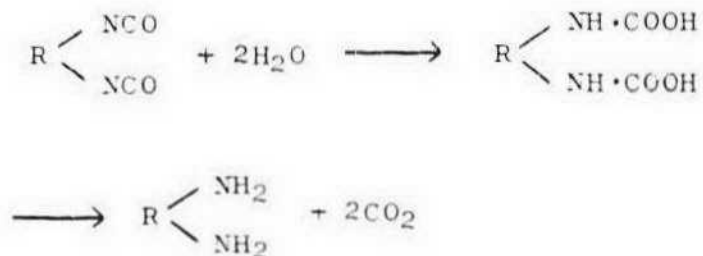
The amine thus produced reacts again with TDI to give polyureas.

$$nR \diagdown \begin{matrix} NH_2 \\ NH_2 \end{matrix} + nR \diagdown \begin{matrix} NCO \\ NCO \end{matrix} \longrightarrow (-NH \cdot R \cdot NH \cdot CO \cdot NH \cdot R \cdot NH \cdot CO-)$$
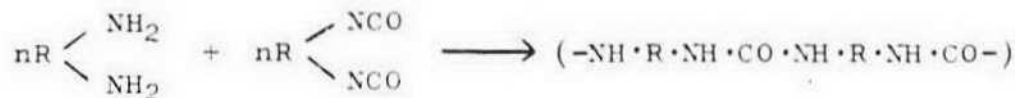
Thus, the possible pollutants in water would be amine and polyureas.
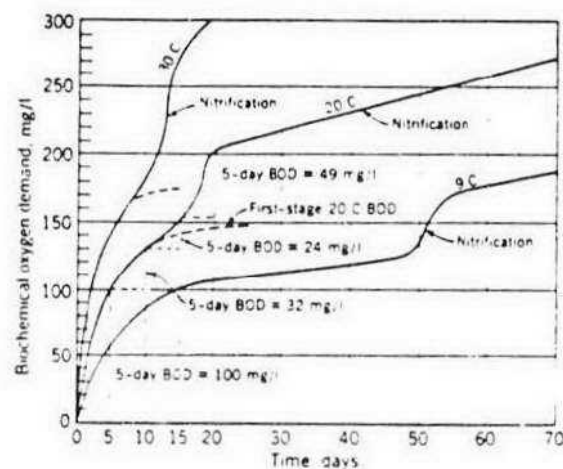
FIG. 1-1 Progress of Biochemical
Oxygen Demand (BOD)
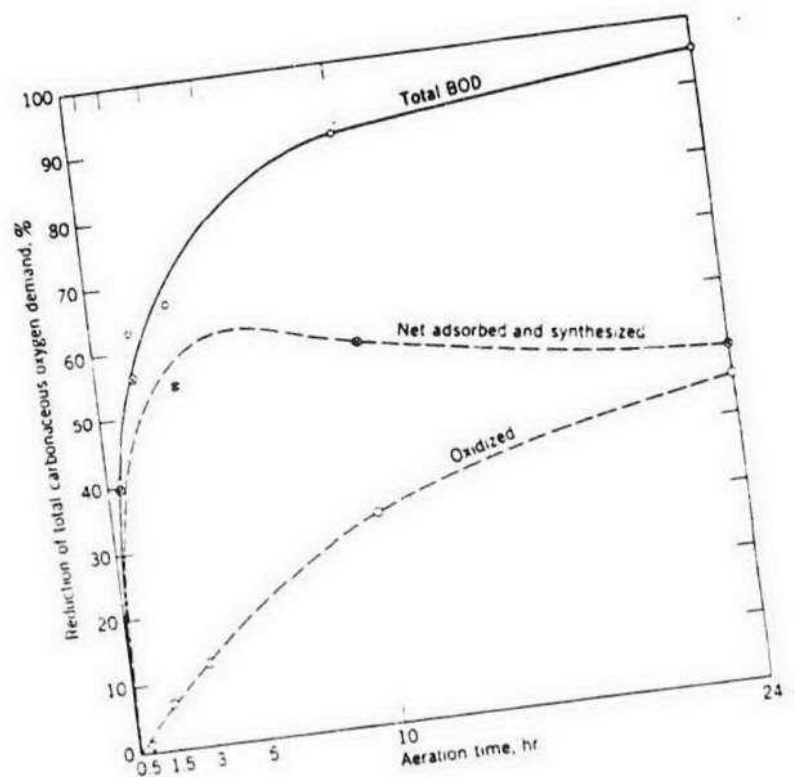
Fig. 1-2. Removal of Organics by Biomass in a Batch Operation
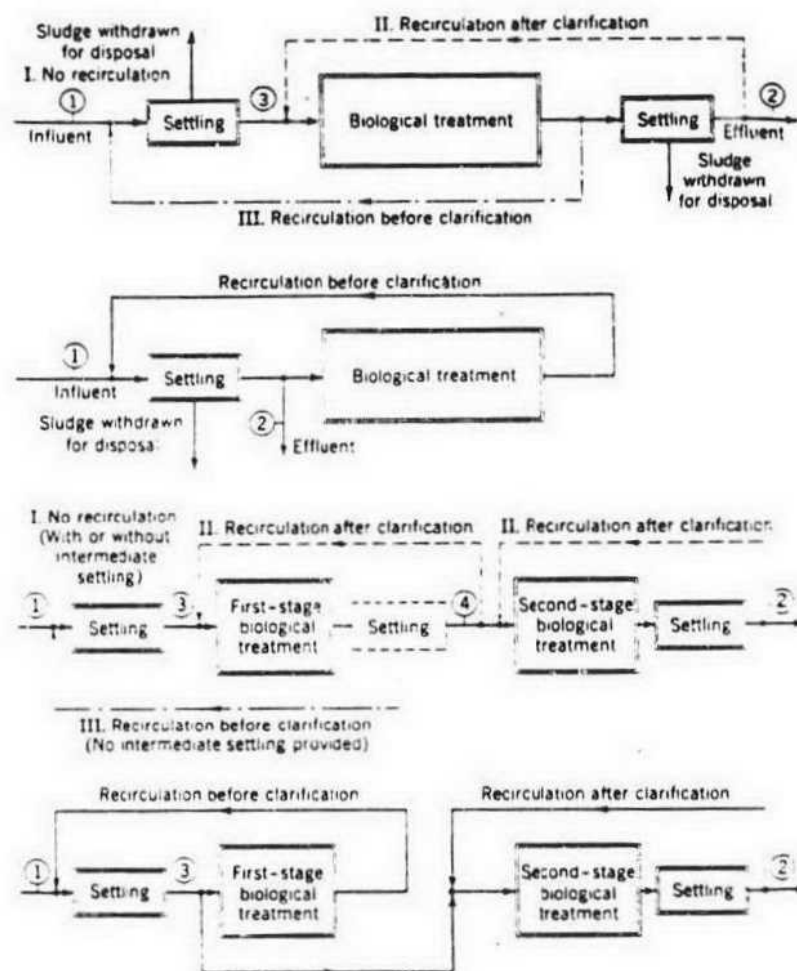
Fig. 1-3 Flow Charts for the Biological Waste Water Treatment System
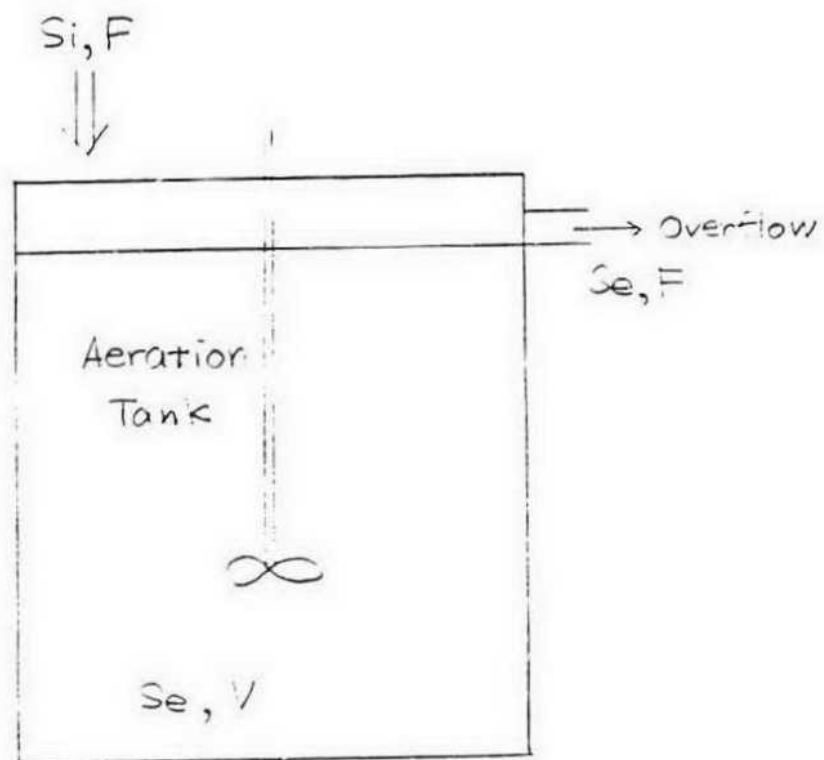
Fig 1.4. Scheme of aeration Tank
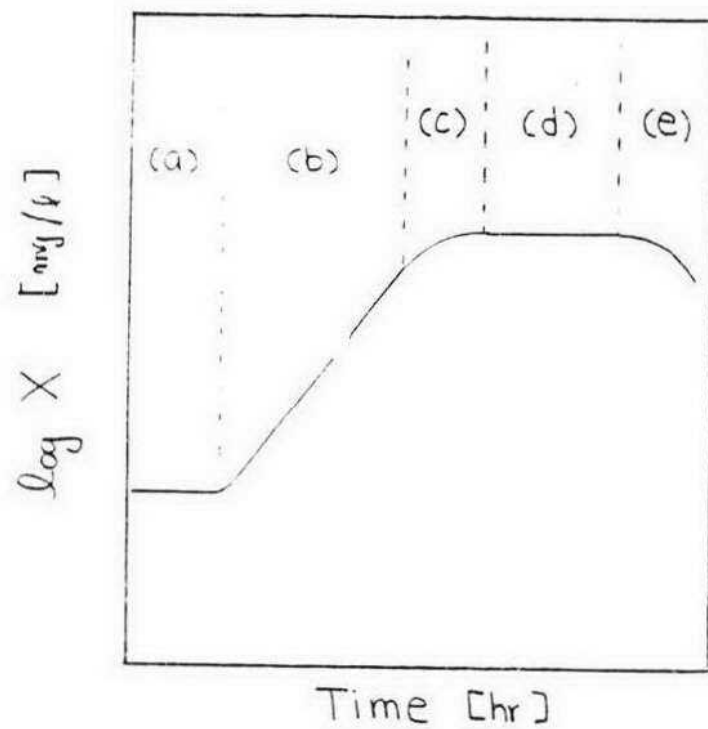
Fig 1.5. Growth phase for batch culture
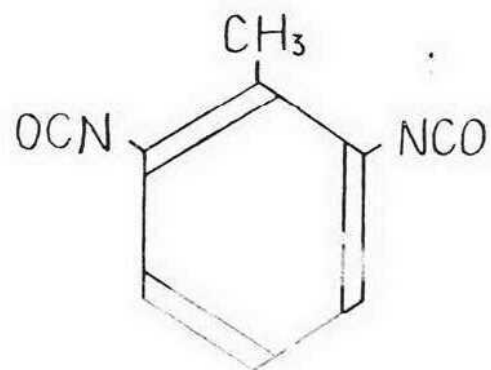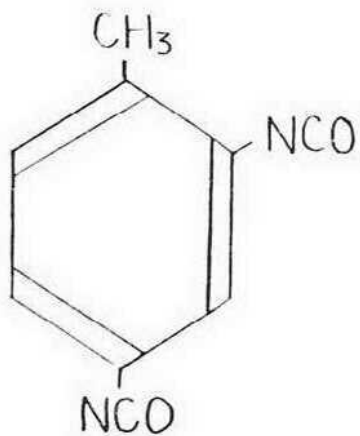
Fig. 1-6. Tolylene   diisocyanate. (TDI)

2. Design and Operation of Model Plant for Activated Sludge

2.1 Preparative Design and Operation of Aeration Tanks

2.1.1 Introduction

For the study of biological waste water treatment, it is important to prepare the well-controled aeration tank. In order to avoid the fail in designing the aeration tank, the small scale preparative experiments (about 13 ^{L} vessel) were made at first. Then, the comparatively large sale vessel was designed being based upon the data obtain in the small scale experiments.

2.1.2 Experimental

Three types of vessels were designed as shown in Fig. 2-1. The parameters associated with culture such as MLSS, SV_{30}, SVI, COD of influent and effluent, were measured according to the methods mentioned previously. The temperature and D.C. in the aeration tank were maintained $25 \pm 2^{\circ}C$ and 0.5 to 2 ppm, respectively. For each vessel, corn-steep-liquor was continuously fed as a substrate.

(A) Results

Figs. 2-1, 2-2, 2-3, 2-4, 2-5 and 2-6 give the original data obtained from the culture vessels I, II, and III, respectively.

(a) Comments for vessel I

As is seen in Fig. 2-2, MLSS increases gradually

and oscillates around 2,500 ppm.

It is known that the activated sludge is stable
for the variety of load at the comparatively high
value of MLSS.

Being based on our experience, the vessel is well
operated at the value of 2,000 - 2,500 ppm.
SVI is as low as 30, regardless of MLSS as shown
in Fig. 2-2. This indicates that the activated
sludge has the good settling character. The
treatability of COD is as high as 90%. As a whole,
good operation was made up to 13th day.
However, on 14th day, activated sludge became
bulking and large amount of sludge was lost. Then,
MLSS decreased rapidly. Immediately after the
bulking phenomenon was found, the feeding of sub-
strate was stopped and the new sludge was added
gradually. To recover up to the normal state of
the aeration tank, about 10 days were needed after
bulking appeared.

(b) Comment for vessel II

As shown in Fig. 2-4, MLSS stays as low as 1,000
ppm and SVI is high judging from this, the oper-
ation seems not to be proper. However, the
treatability is above 80% and stable. This suggests

that SVI and MLSS are not always convenient para-
meters for the treatability.

(c) Comment for vessel Ⅲ

In this case, F/M was fractuated with time.
MLSS decreased gradually and pH stayed at rela-
tively high values. Treatment efficiency was
also not stable.
The relations between parameters are not obtained
directly from experimental data.

2.1.3 Discussions

The data obtained directly does not give the understanding
for the operations of aeration tank. Then, a few trials
to deduce the correlations between parameters and funda-
mental understanding of the microbial ecosystem.

(A) Correlation between SVI and MLSS

In Figs. 2-8, 2-9, and 2-10 SVI is plotted vs. MLSS.
For the vessel I (Fig. 2-8) SVI stays constant, regard-
less of MLSS and its value is as low as 30.
This indicates that the settling character of sludge
is always stable. On the other hand, in Fig. 2-9, SVI
increased for the low value of MLSS.
This indicates that the settling character is not
stable for the growth of activated sludge. In con-
clusion, the stable feeding of substrate (constant F/M)

gives the excellent settling character independently
of the growth of the activated sludge.

(B) Correlation between SVI and F/M

SVI vs. F/M is plotted in Figs. 2-11, 2-12, 2-13.
In Fig. 2-11, and 2-12, SVI decreases with F/M as long
as F/M is less than 0.15, while it increases again for
the higher value of F/M than 0.2. This shows that when
F/M is low the sludge is light and that the optimum
value of F/M exists to obtain good settling character.

(C) Correlation between treatment efficiency and F/M

The correlation between treatment efficiency and F/M
appears in Figs. 2-13, 2-14, 2-15 for vessel I, II,
and III, respectively. In the cases of vessel I, and
II, treatability increases with F/M, while in the case
of vessel III, the maximum is observed. In the vessels
I and II, the loading was so low as the substrate which
could be oxidized biologically was almost treated.
It is estimated for the vessel III that the decrease
in treatability for the value of F/M higher than 0.15
appeared due to the excess loading the treatable limit.
It should be recognized that the optimum value of F/M
exists clearly and treatment efficiency is affected by
F/M sensitively.

2.2   Design and Operation of Model Plant

2.2.1   Introduction

Being based on the data obtained from the small scale
experiments the comparative large model plant of aeration
tank was designed and operated. The operating data for
20 days and their analysis are presented in the chapter.

2.2.2   Design of the vessel

The geometry of the designed vessel is shown in Fig. 2.17.
The aerobic reaction proceeds in the central space and
water circulate according to the arrow. The small space
in the left side is prepared to separate the water from
sludge.

2.2.3   Results for the culture of a short period

The parameters associated with culture for 20 days oper-
ation are plotted in Figs. 2-18, 2-19, 2-20, and 2-21.
As is shown in Fig. 2-18, MLSS increased with oscillation
and attained the steady states after about 10 days. The
initial value of MLSS was 1,250 mg/ and that after 10
days was 2,000 mg/ .

The vessel was so operated as MLSS stayed between 2,000
mg/ and 3,000 mg/ . SVI stayed almost constant as much
as 30-40 after 7 days operation regardless of the increase
in MLSS.

This indicates the good operation of aeration tank. As

seen in Fig. 2-21, COD of the effluent was almost constant
throughout the operation independently of COD of the in-
fluent. Thus, the capacity was proved to be large enough
to bear the load given in this experiments. From this
speculation, the organic compounds in the effluent were
not to be biologically active. This is consistent with
the fact that F/M stayed mainly at the value of 0.07 to
0.1 and did not exceed 0.20. Therefore, it is concluded
that the treatability obtained in this experiment is the
maximum for the degradation of corn-steep-liquor. The
oxidation-reduction potential in Fig. 2-20 is kept above
100 mV vs. NHE except for 2nd day. The system was in
aerobic conditions throughout the experiments. pH is kept
between 7.21 and 6.65.

This also indicates the aerobic nature of the system.
Dissolved oxygen was maintained between 0.5 and 2 ppm
except for second and 11th day. If the aeration is too
strong, the system would result in the decrease in pH and
dispersion of floc.

2.2.4 Discussions on the culture for a short period

Correlation between F/M and treatability is given in Fig.
2-21.

As already mentioned before treatability increases with
F/M as long as treatability limit is not exceeded.

This figure clearly showed this tendency. From Fig. 2-22 maximum treatability for corn-steep-liquor seems to be about 90%.

So far as the present experiment concerned the activated sludge system was not over-loaded. The correlation between ORP and F/M is examined in Fig. 2-23. ORP seems to show a maximum around F/M = 0.10, where the system might be most aerobic. ORP is also plotted against treatability in Fig. 2-24. Generally, it seems that the activated sludge treats the organic matters efficiently when ORP is high. It is concluded that the degradation of organic compound would proceed more efficiently as the environment is more aerobic.

2.2.5 Culture for long periods

The activated sludge has been acclimated with corn-steep-liquor under the conditions of continuous culture in the pilot plant (vessel IV).

The parameters given and obtained are plotted in the same manner as before. The activated sludges used for the experiments were taken from the system thus acclimated. Therefore, the history and conditions of activated sludges used for the experiment can be obtained precisely if necessary. They appear in Figures 2-25 to 2-72.
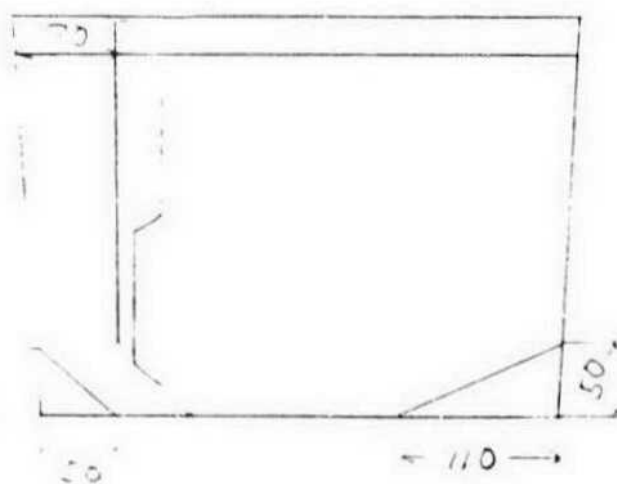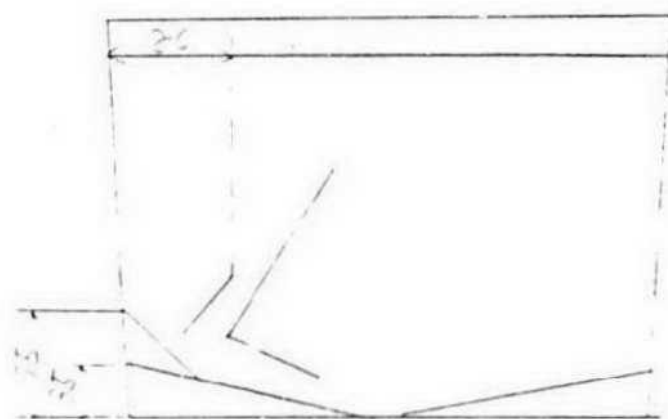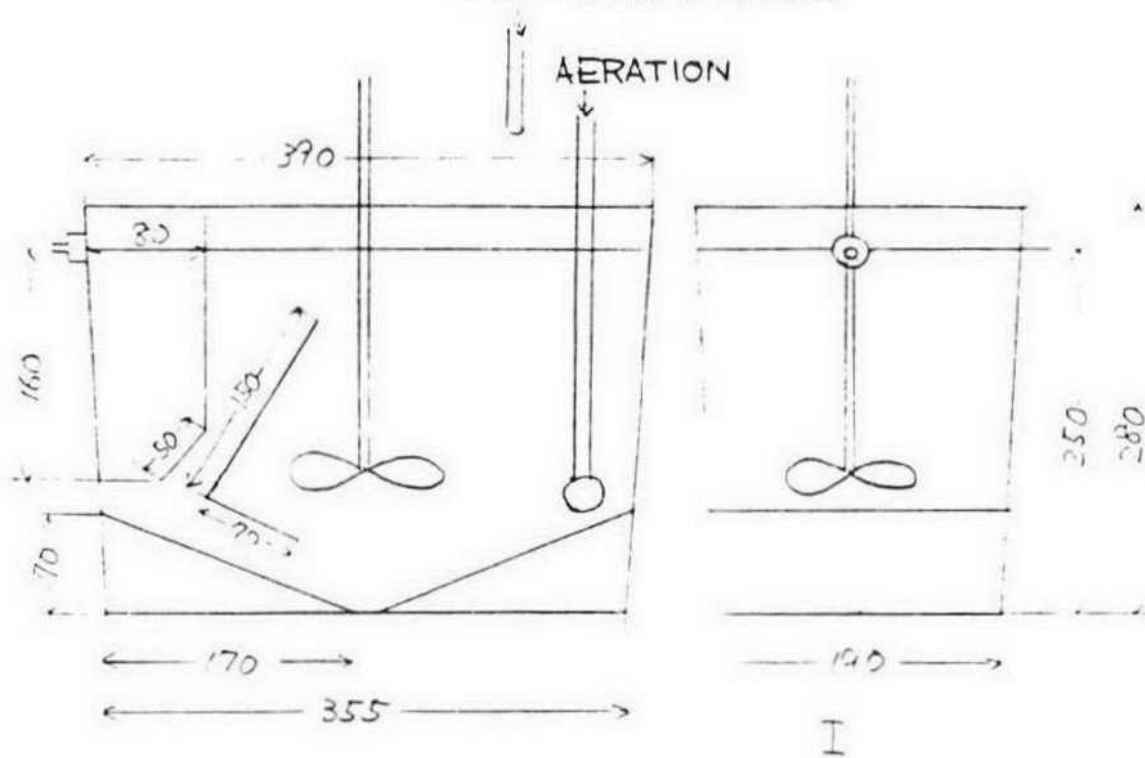
Fig 2-1. THREE TYPES OF VESSELS
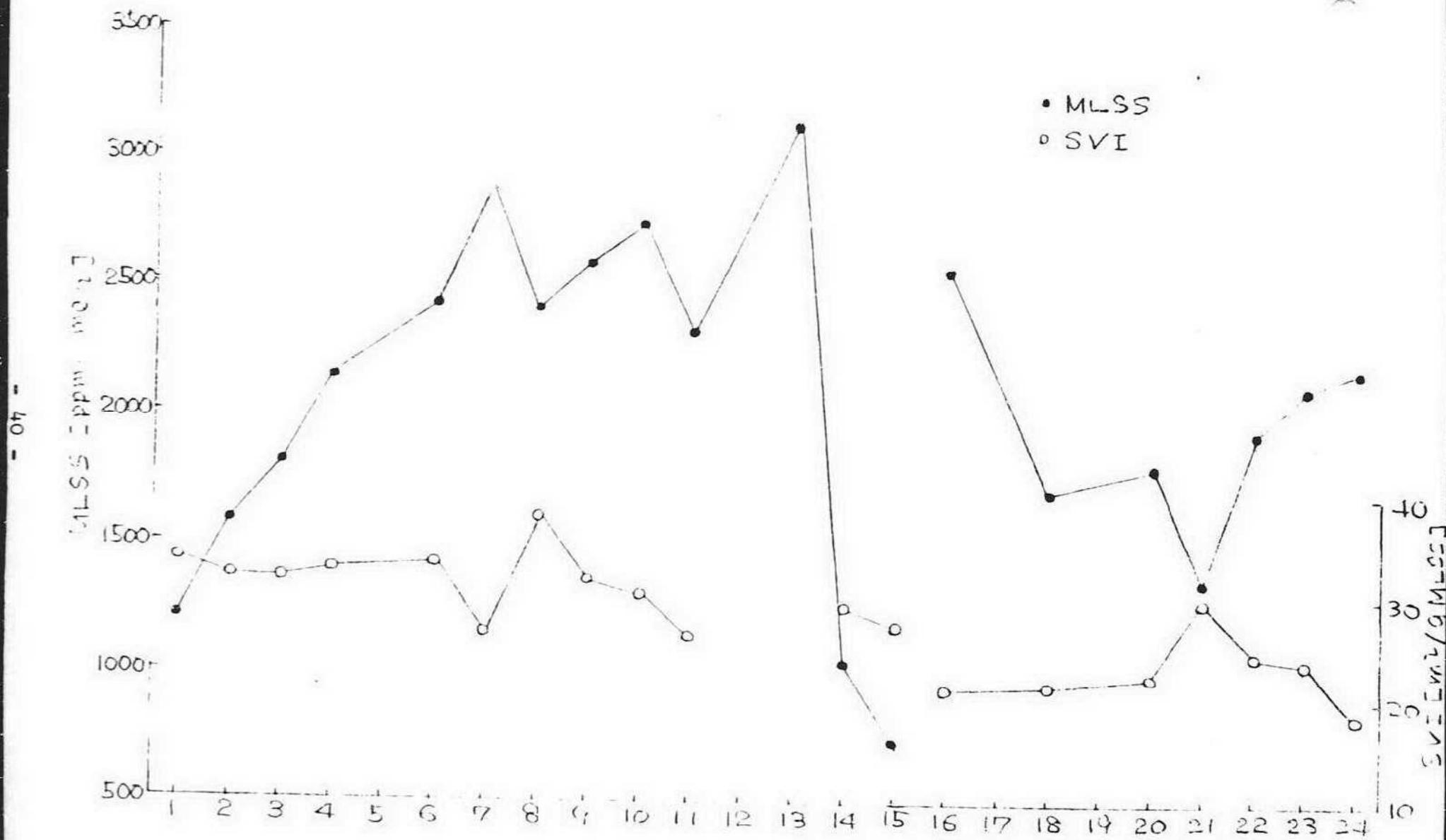
Fig.2-2. MLSS and SVI (Vessel I)
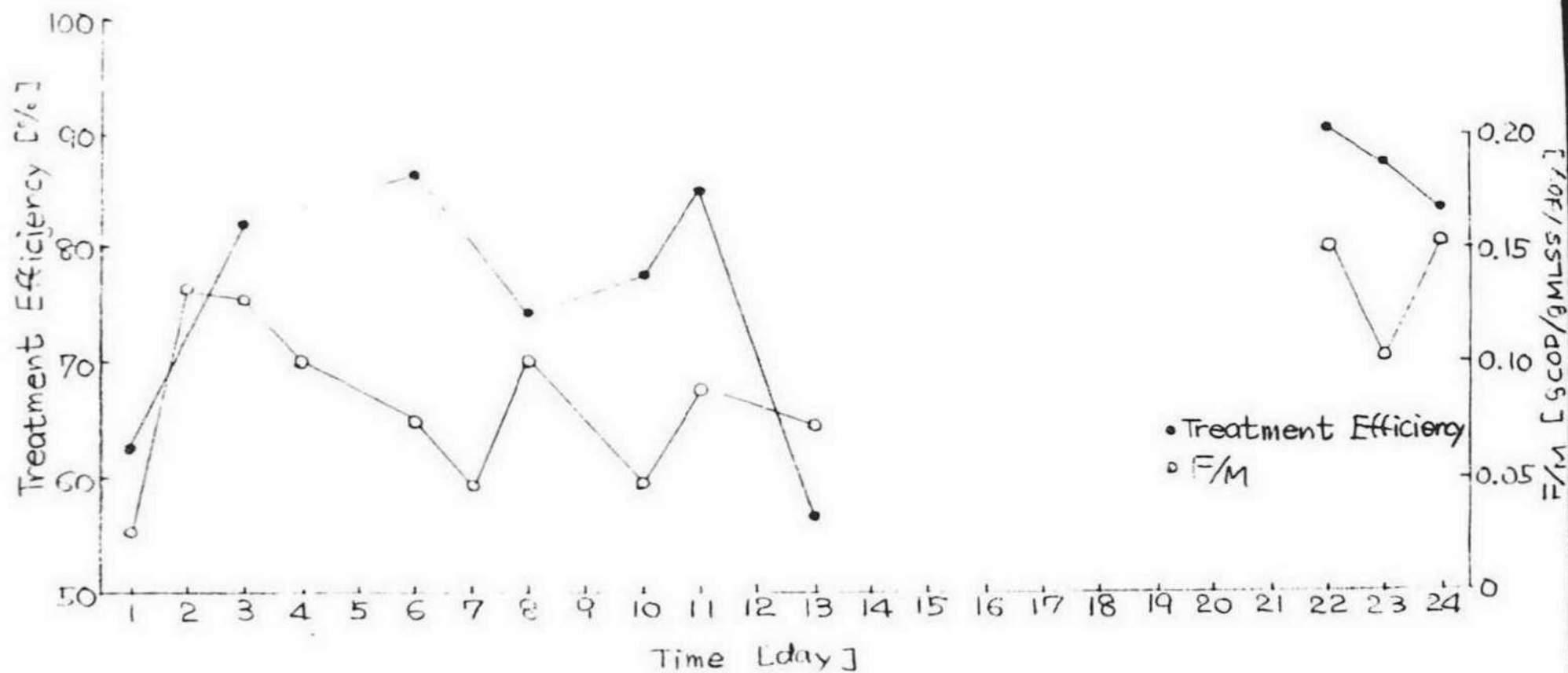
Fig 2.3 Treatment Efficiency and F/M (Vessel I)
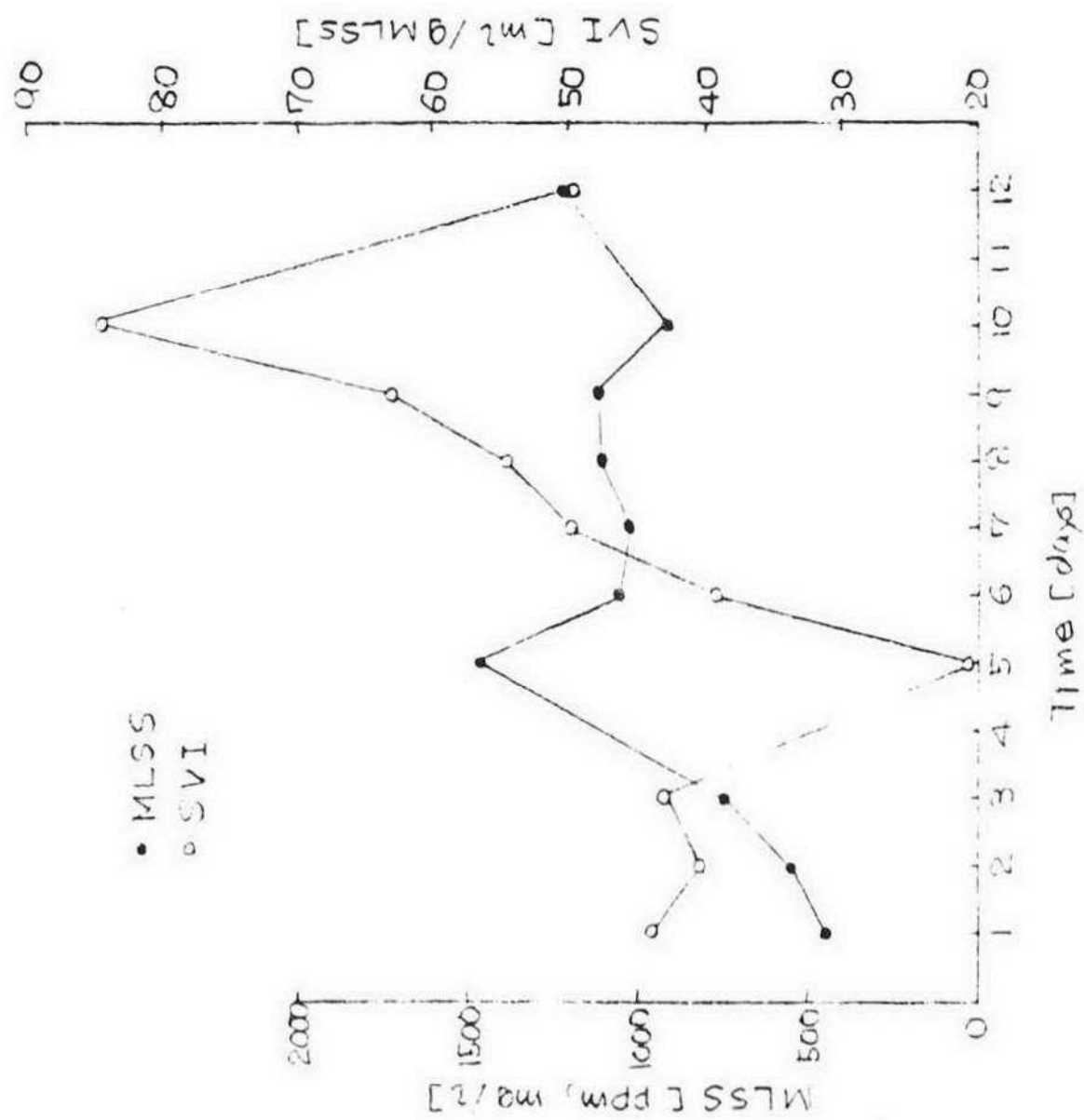
Fig. 2.4. MLSS and SVI (Vessel II)
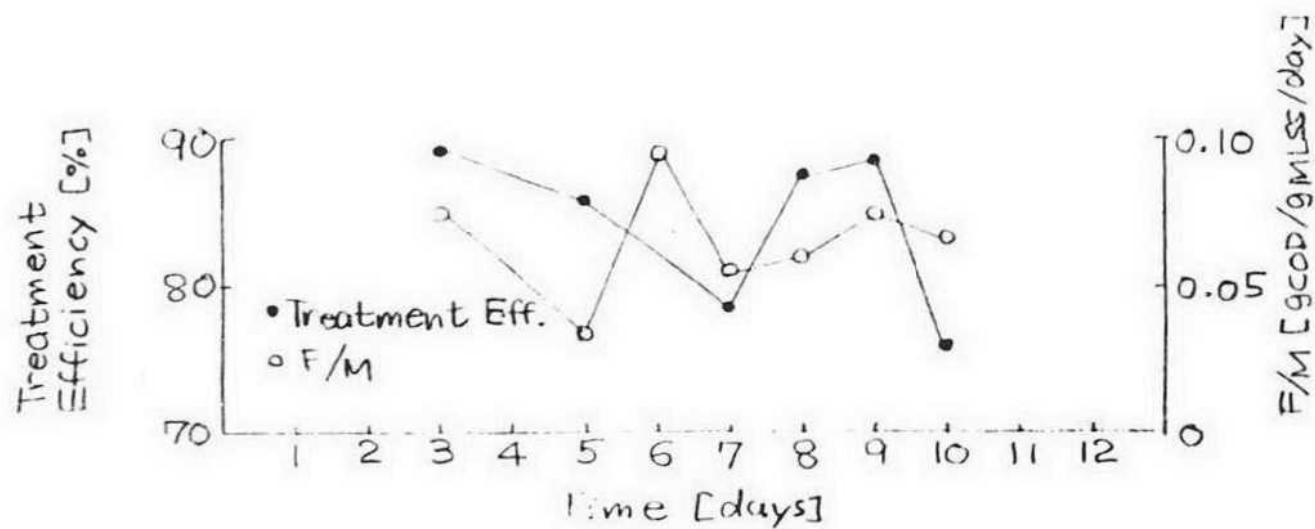
Fig. 2-5 Treatment Efficiency and F/M (Vessel II)
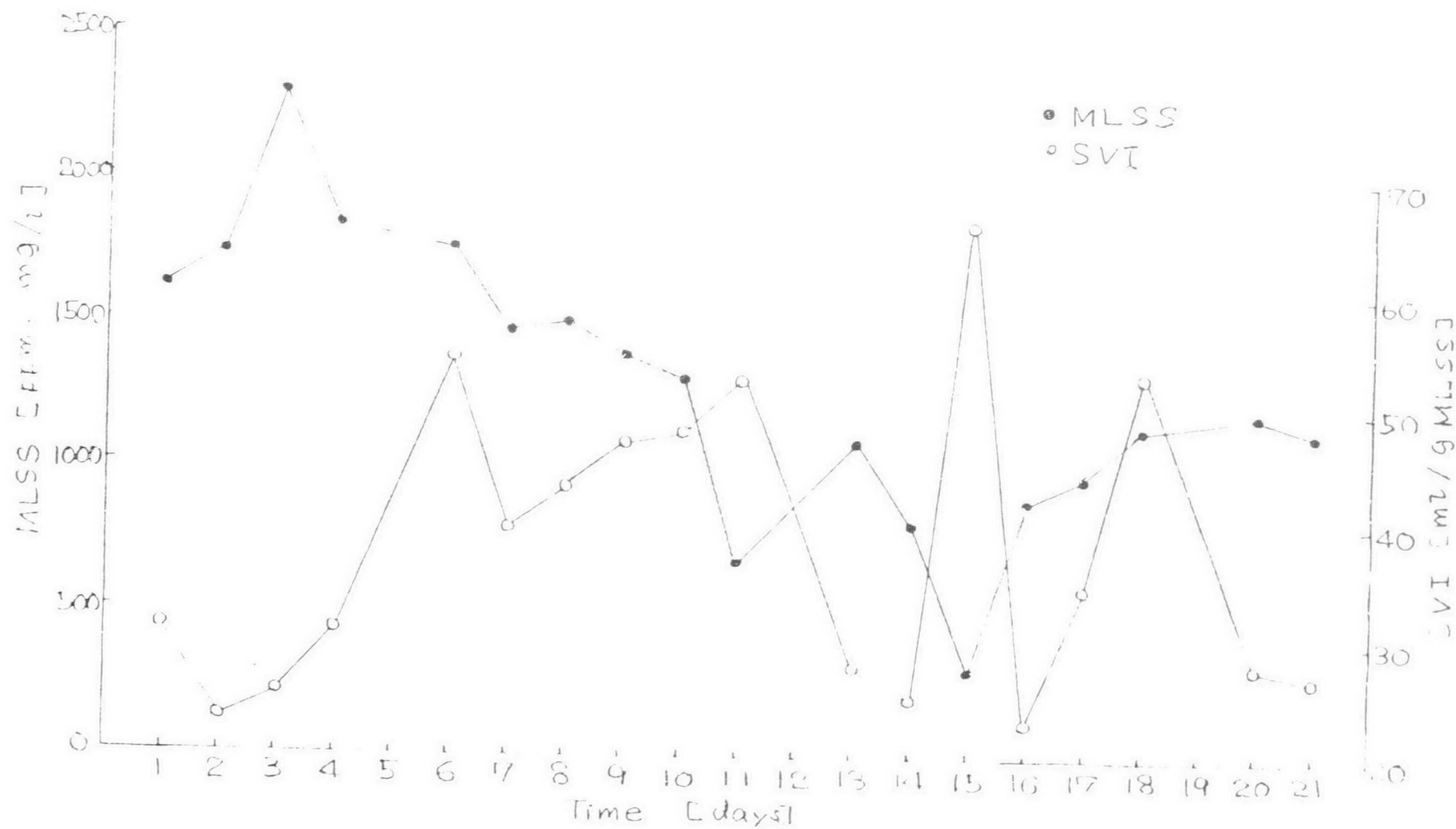
Fig. 2-6. MLSS and SVI (Vessel III)
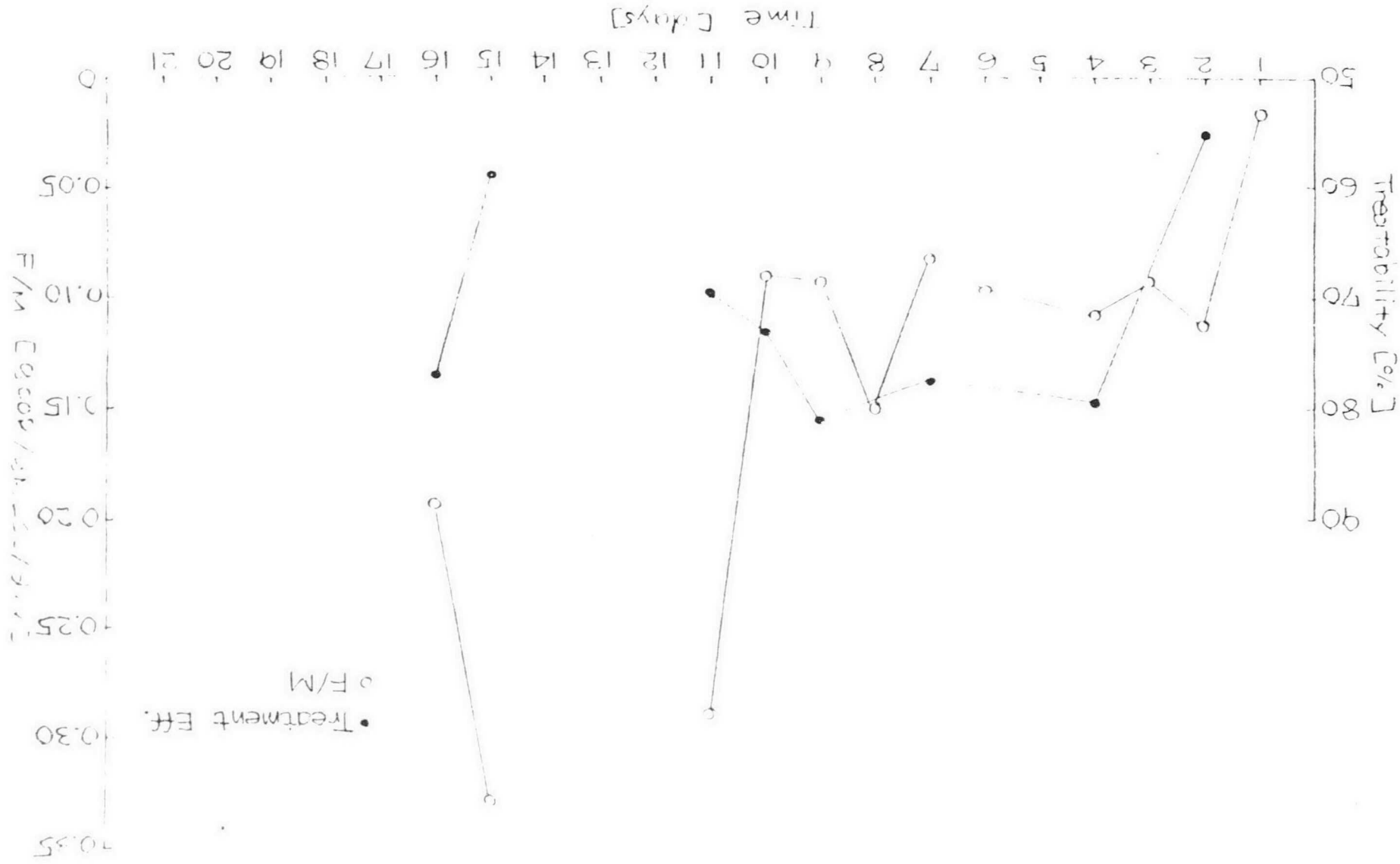
Fig. 2-7 Treatment Efficiency and F/M (Vessel III)

Time [days]

F/M [gCacod/g...]

Treatability [%]

Treatment Eff.

F/M
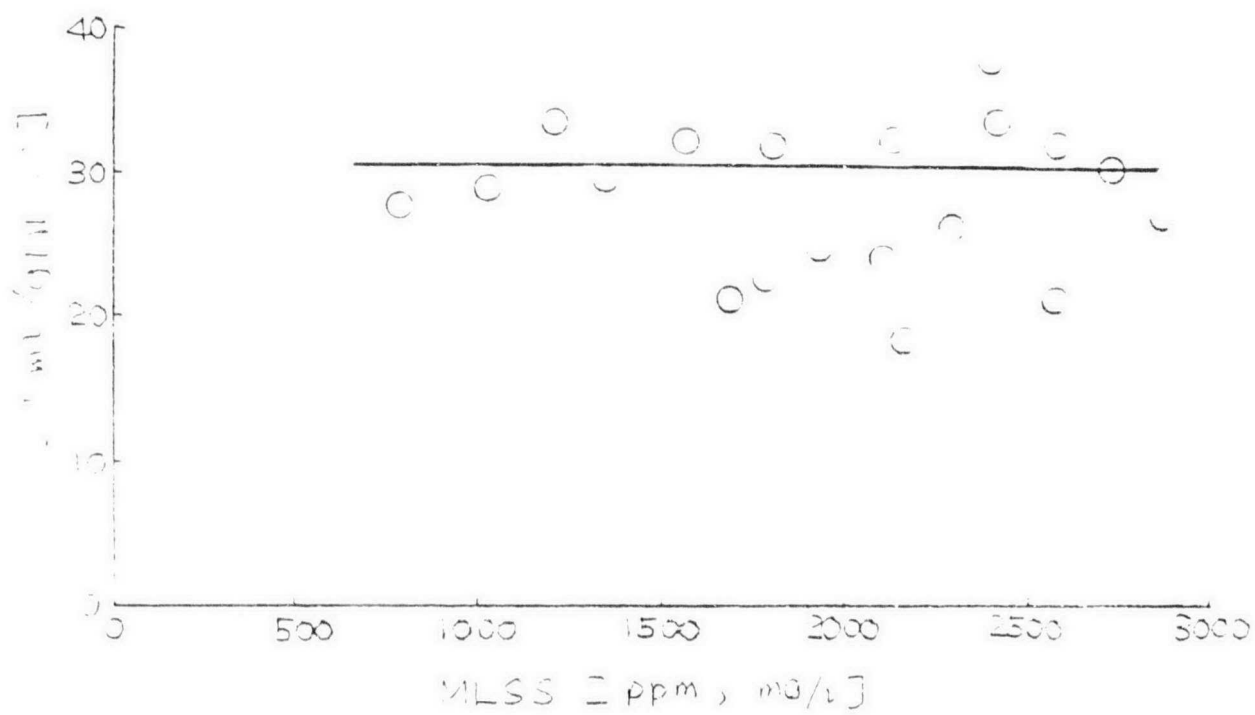
Fig.2-3. Correlation between SVI and MLSS for vessel I
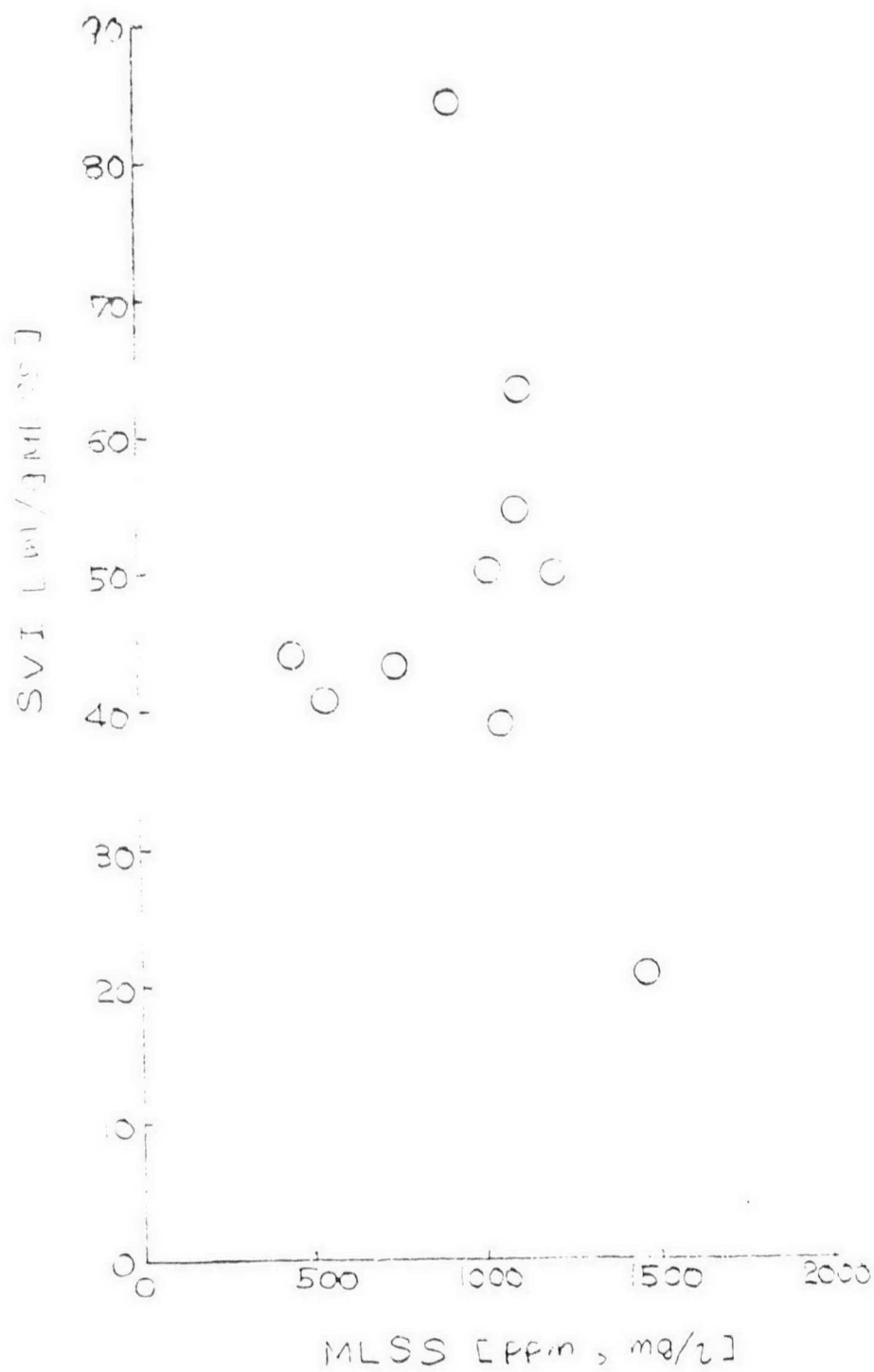
Fig.2-9. Correlation between SVI and MLSS to vessel II
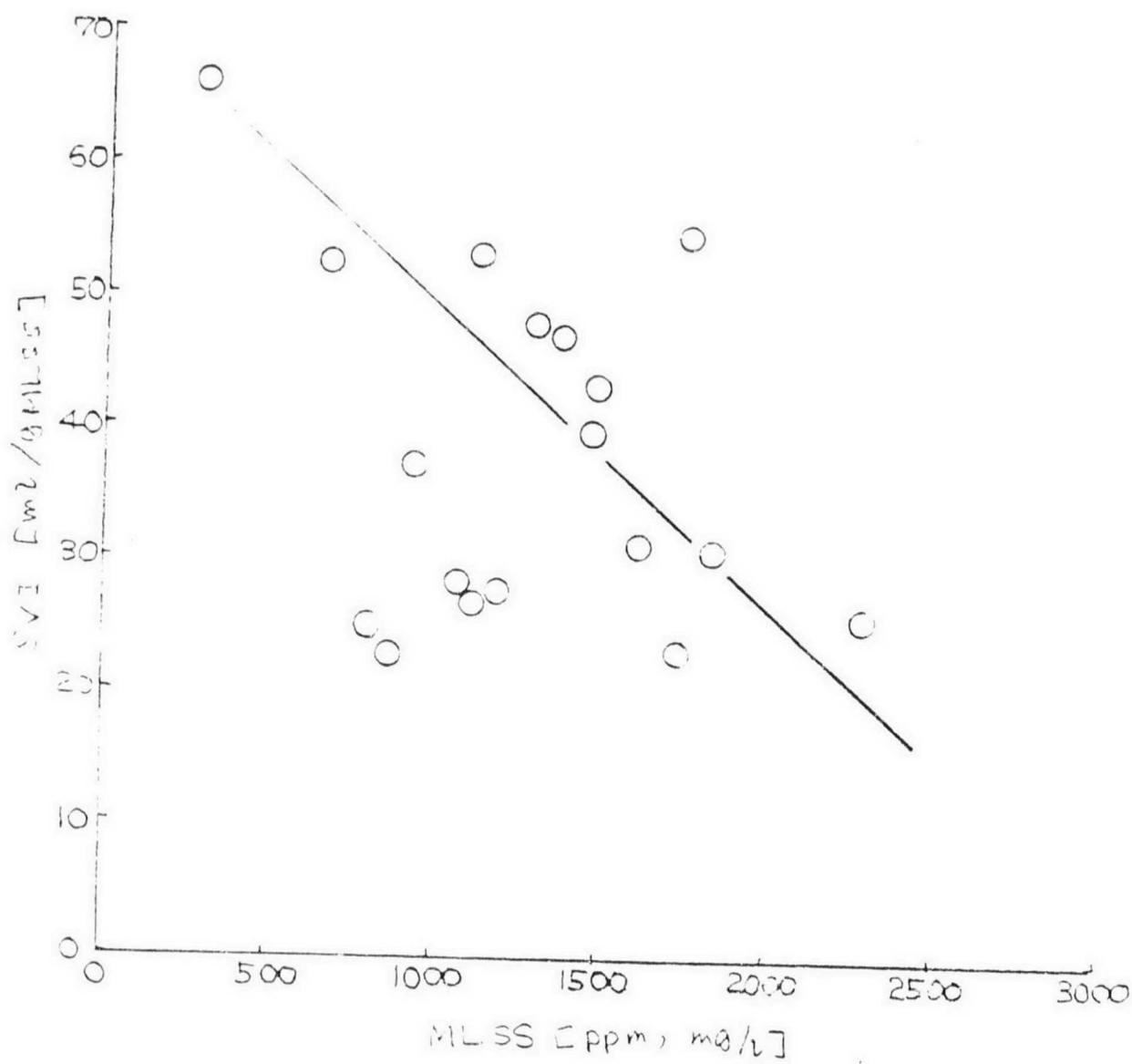
Fig. 2-10. Correlation between SVI and MLSS for vessel III
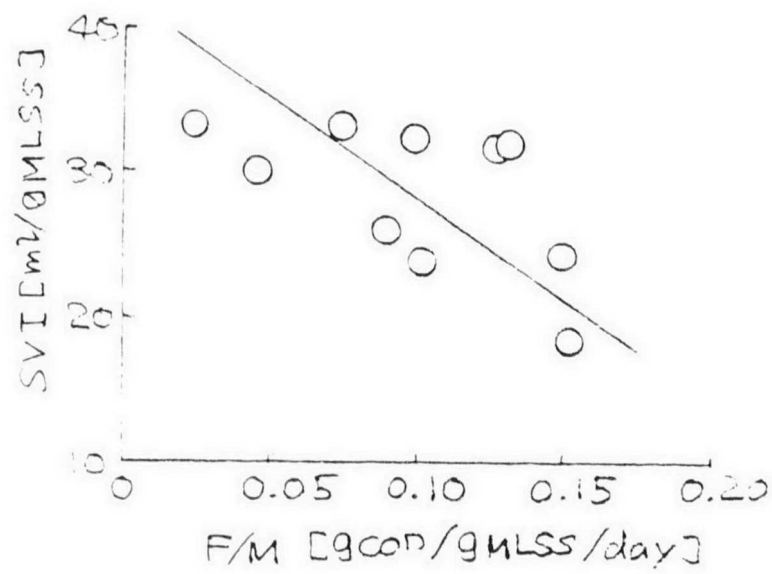
Fig. 2-11. Correlation between SVI and F/M for vessel I
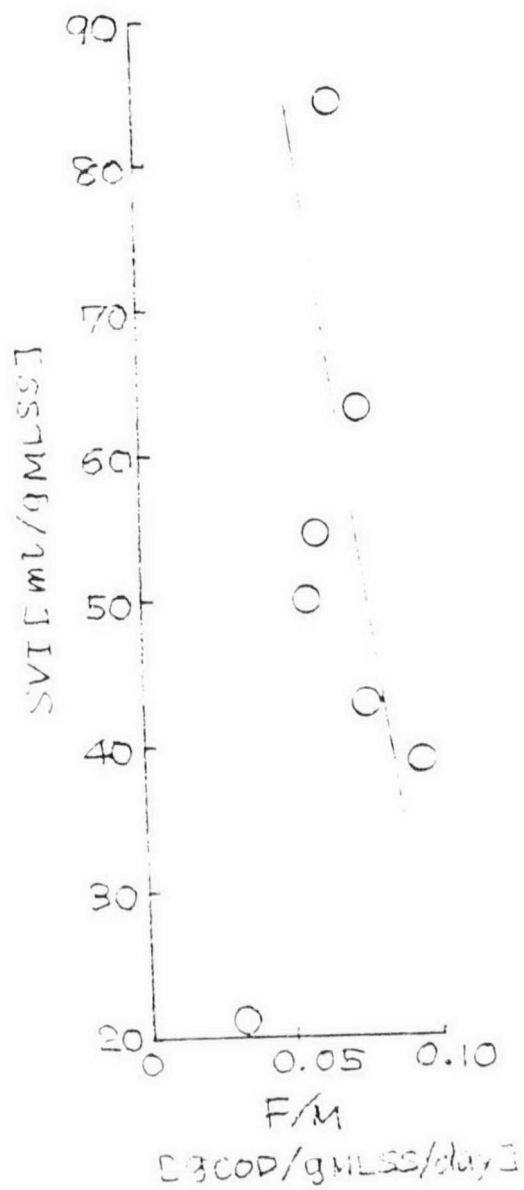
Fig. 2-12. Correlation between SVI and F/M for vessel II
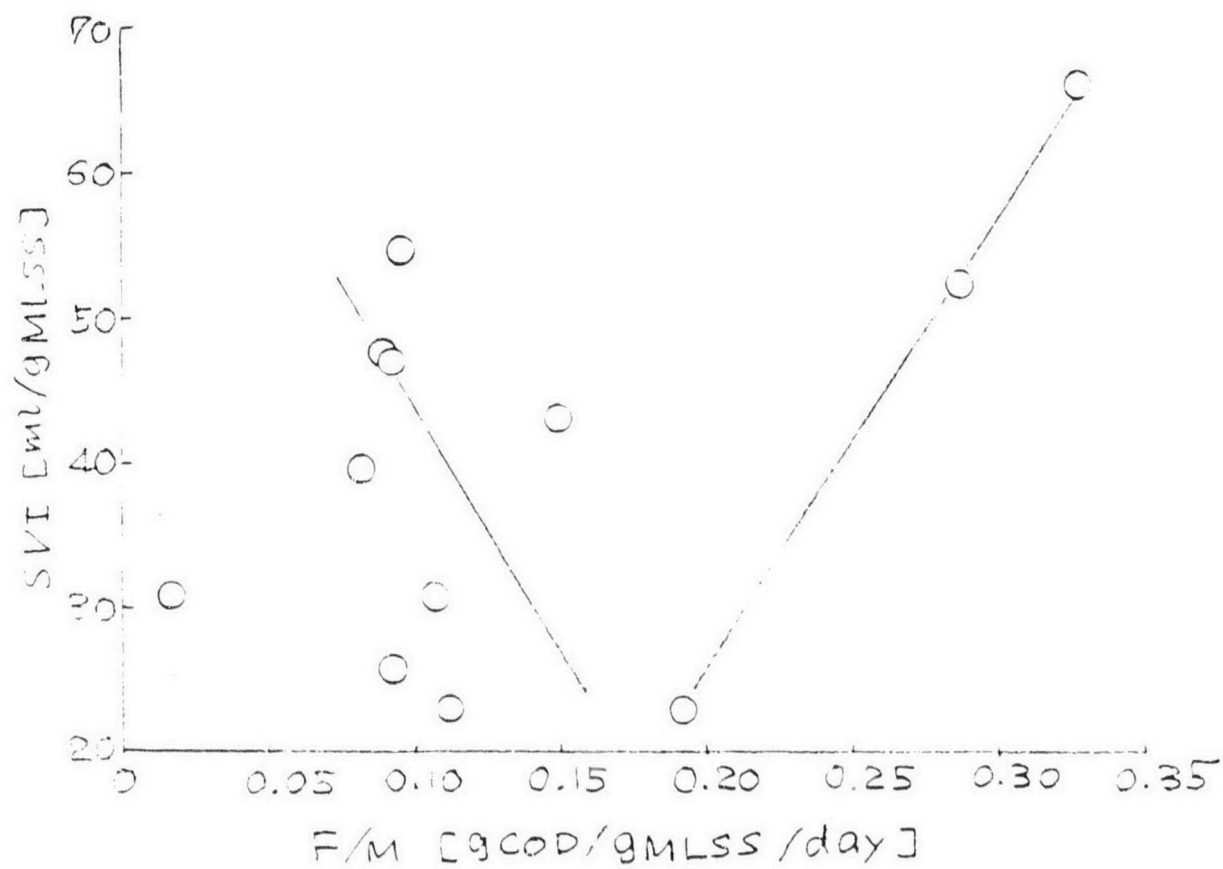
Fig. 2-13 Correlation between SVI and F/M for vessel III

- 51 -
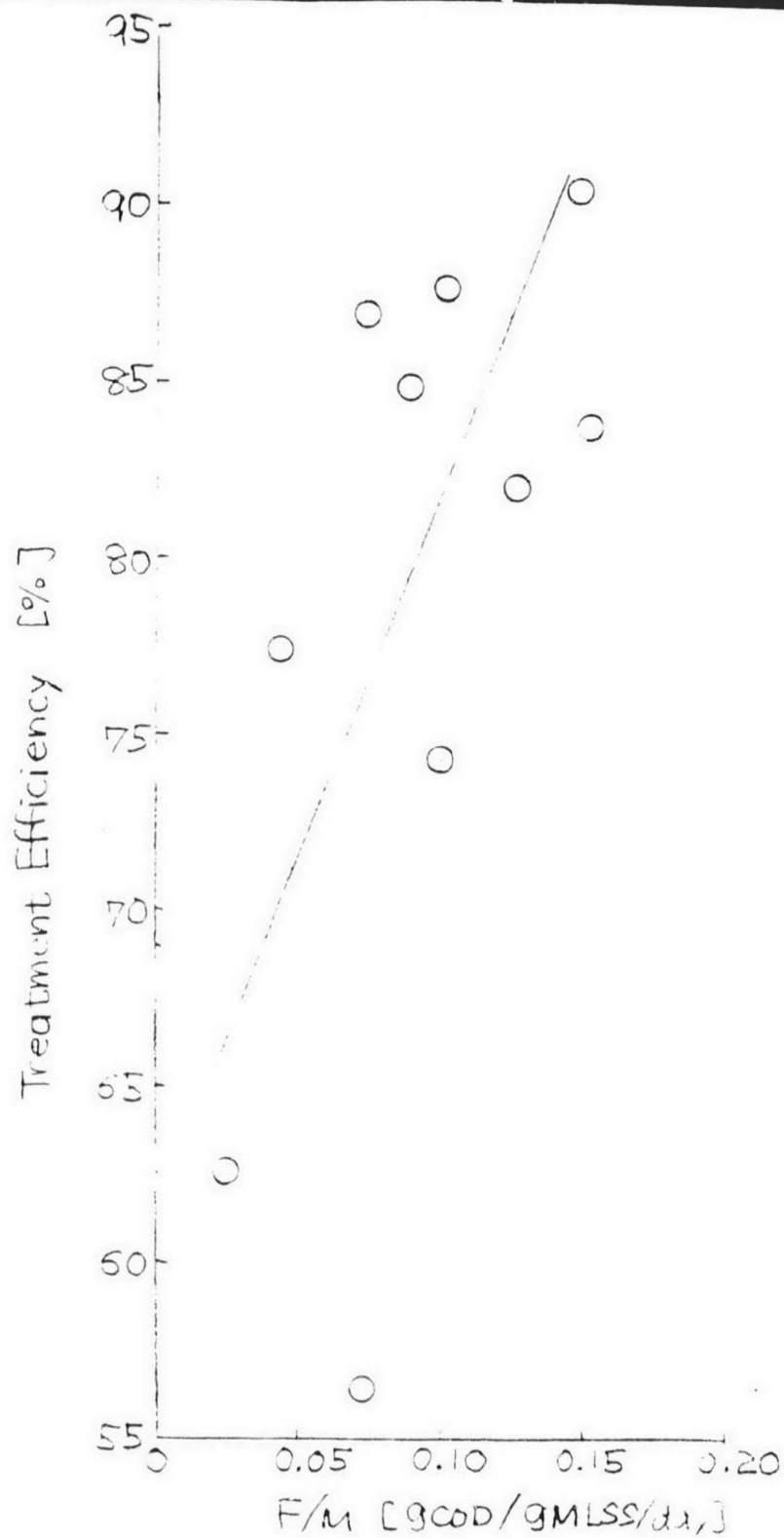
Fig.2-14. Correlation between treatment efficiency and F/M for vessel I
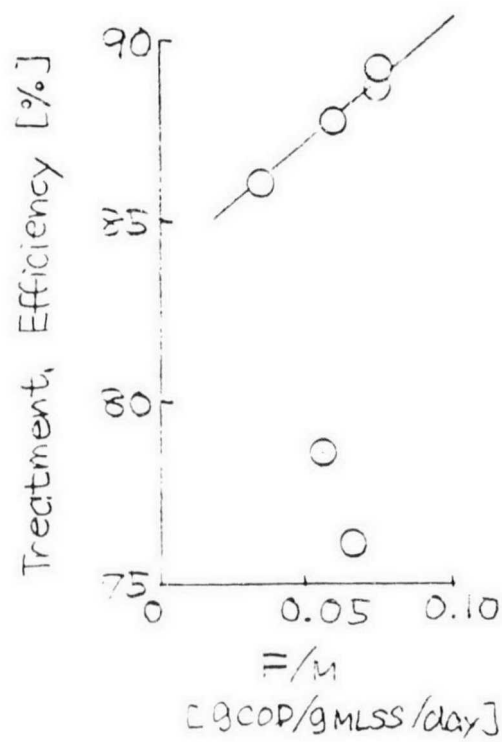
Fig.2-15. Correlation between treatment efficiency and F/M for vessel II
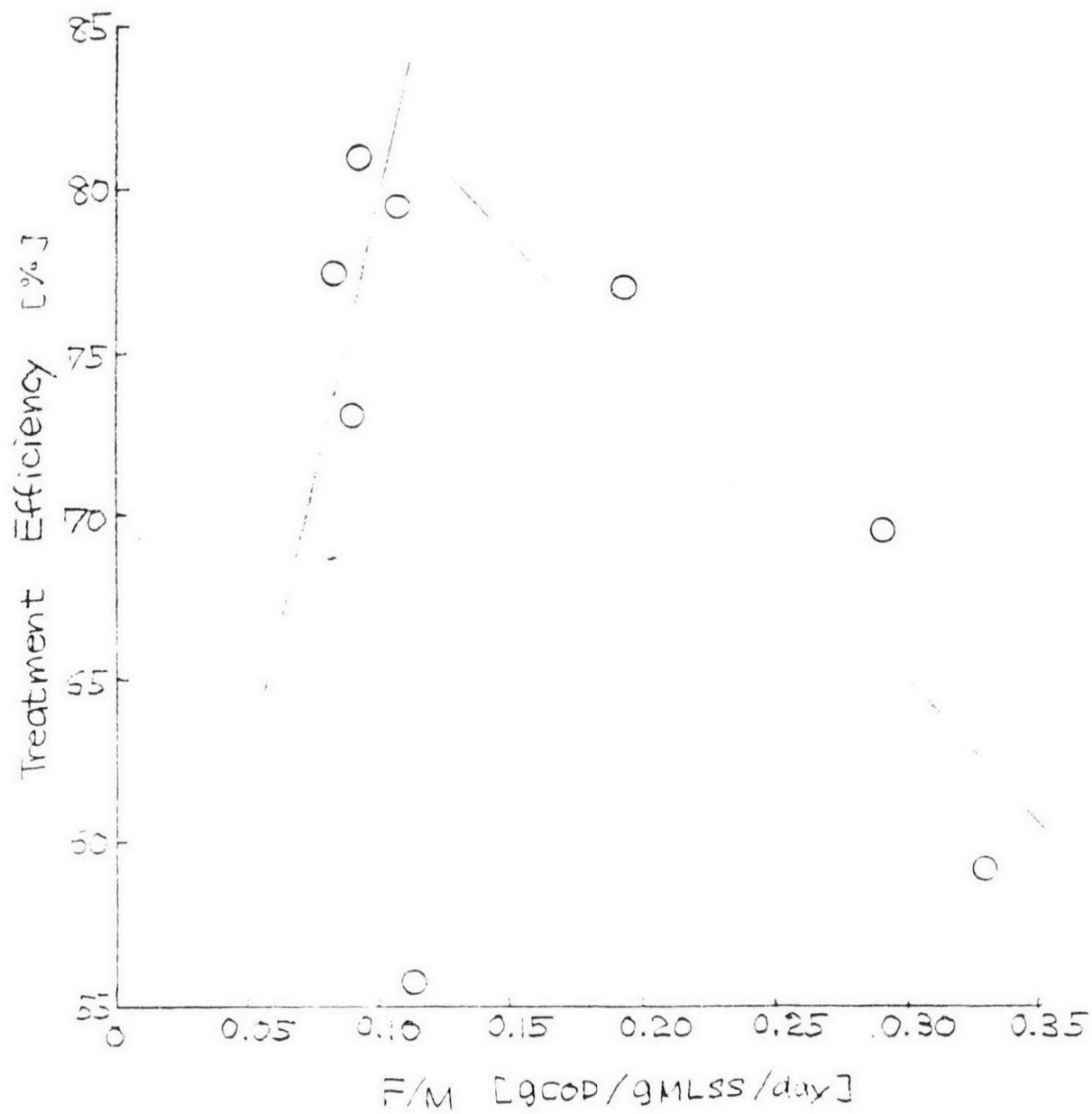
Fig.2-16. Correlation between treatment efficiency and
F/M for vessel III

Overflow

50

385

240

122

440

440

Dimension in mm
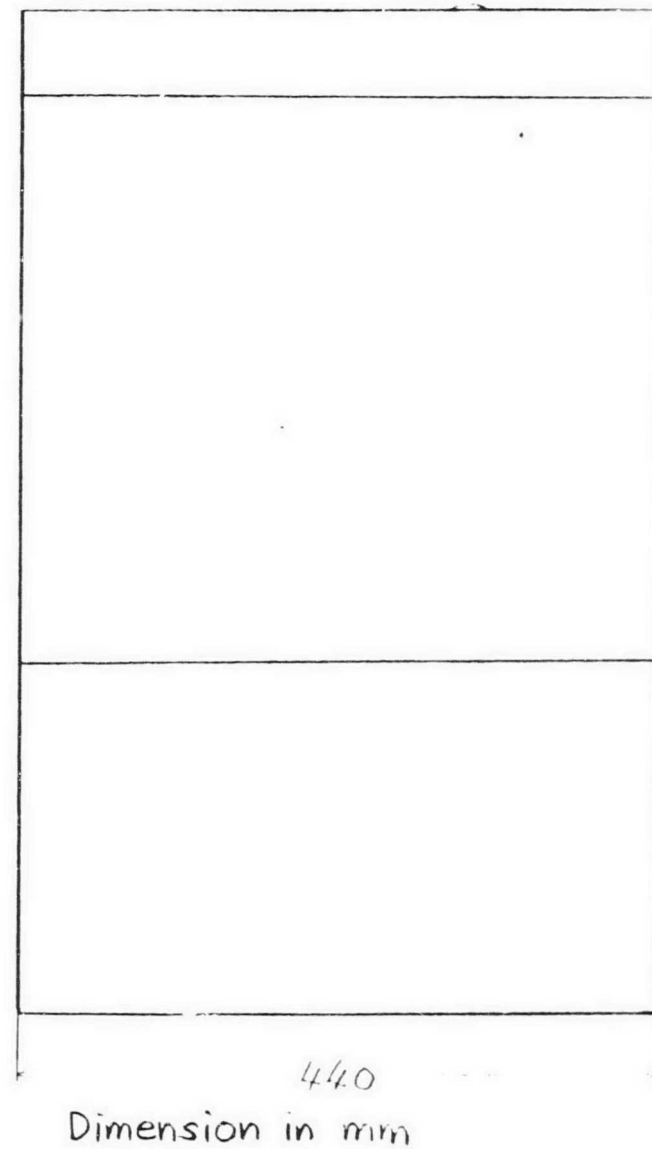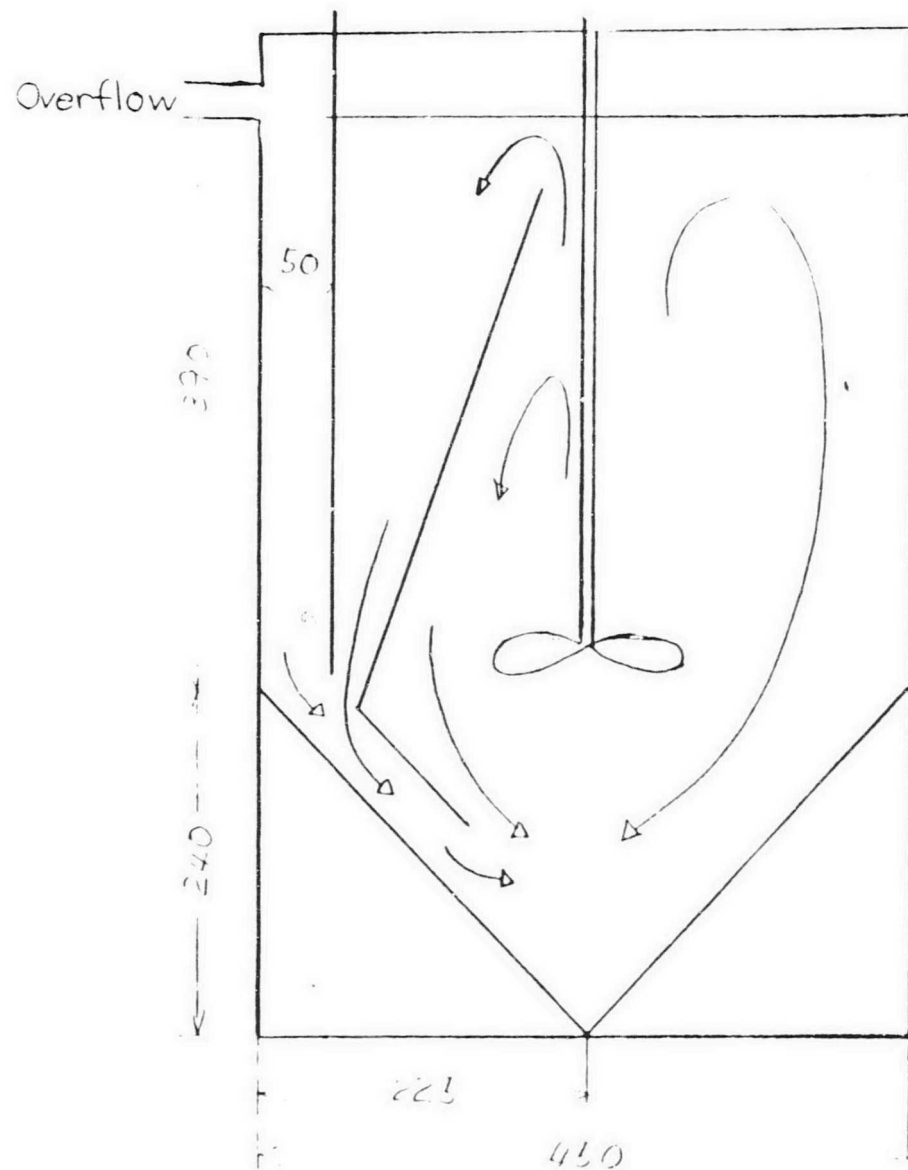
Fig 2-17 Design of Model Plant (Vessel IV)
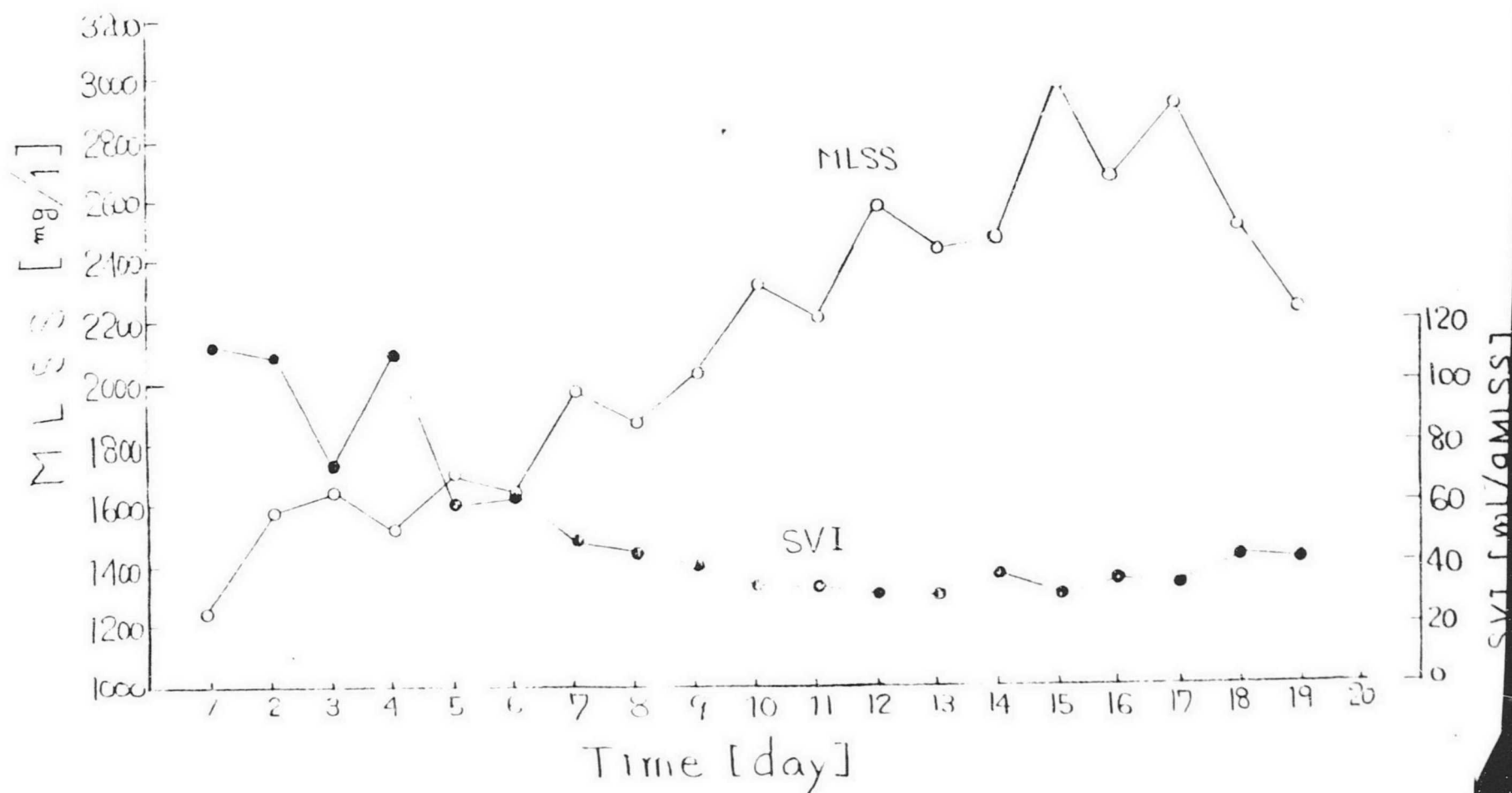
Fig. 2-18   MLSS and SVI
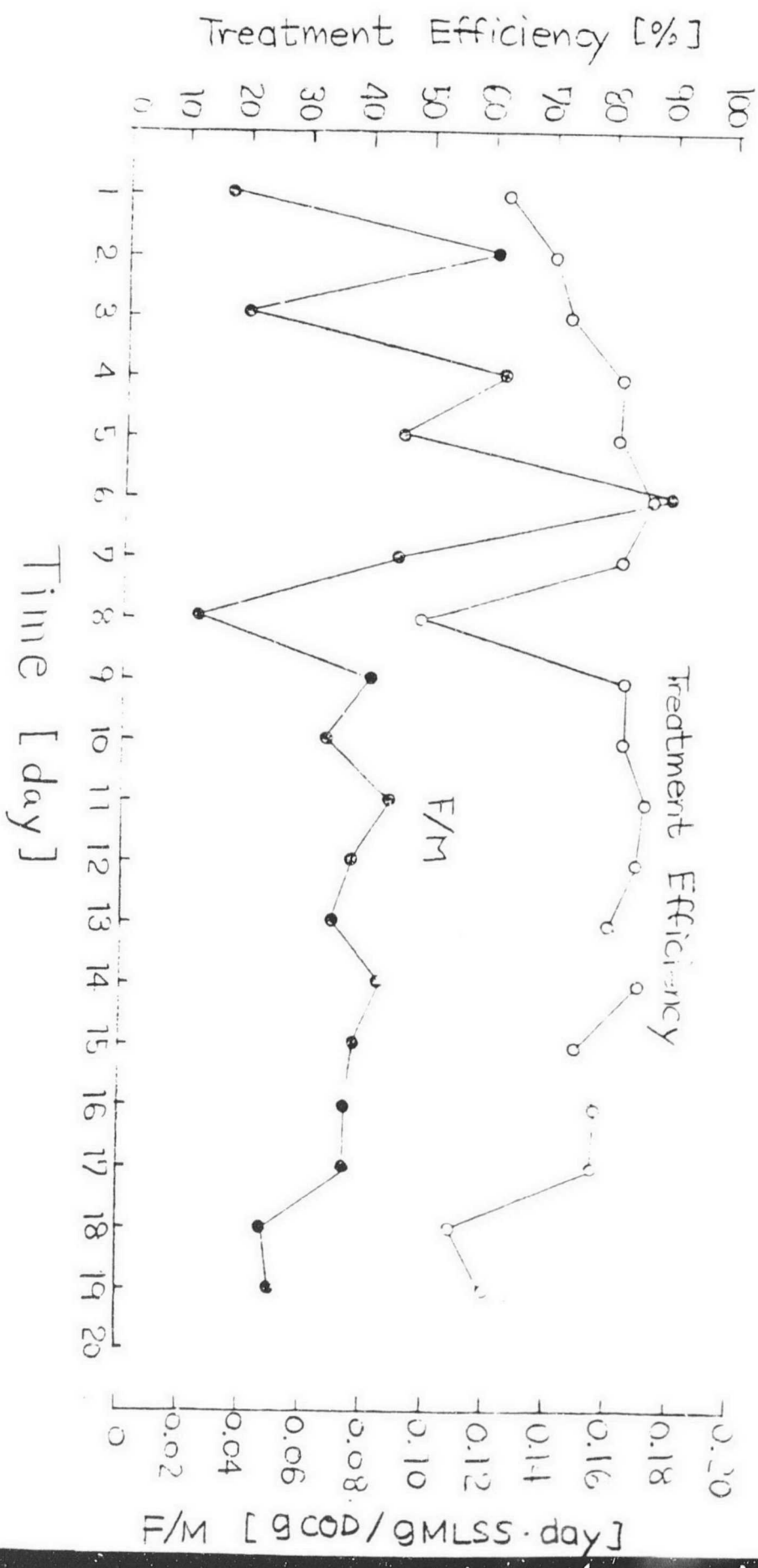
Fig 2-19 Treatment Efficiency and F/M
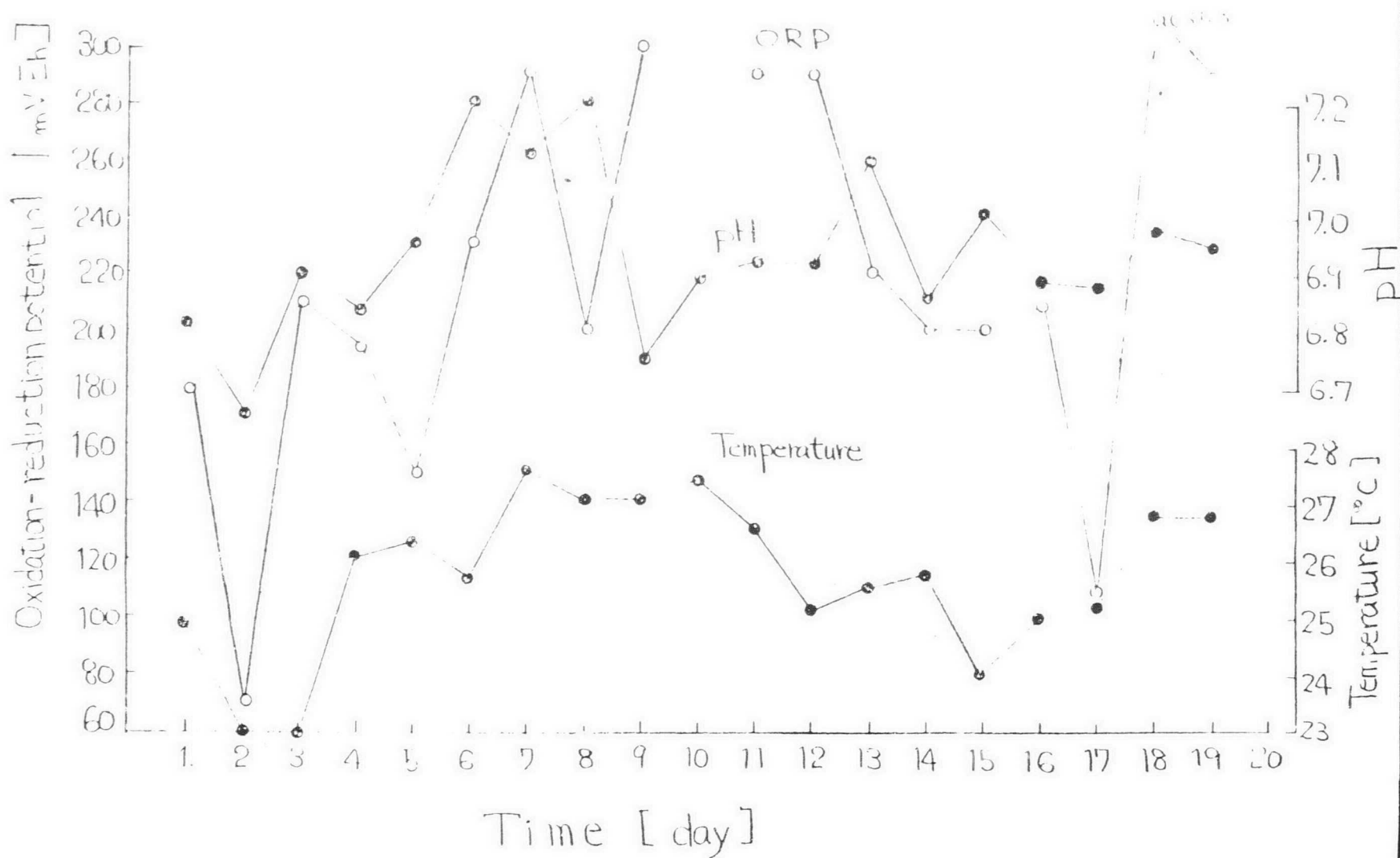
Fig. 2-20 Oxidation-reduction potential, Temperature, and pH
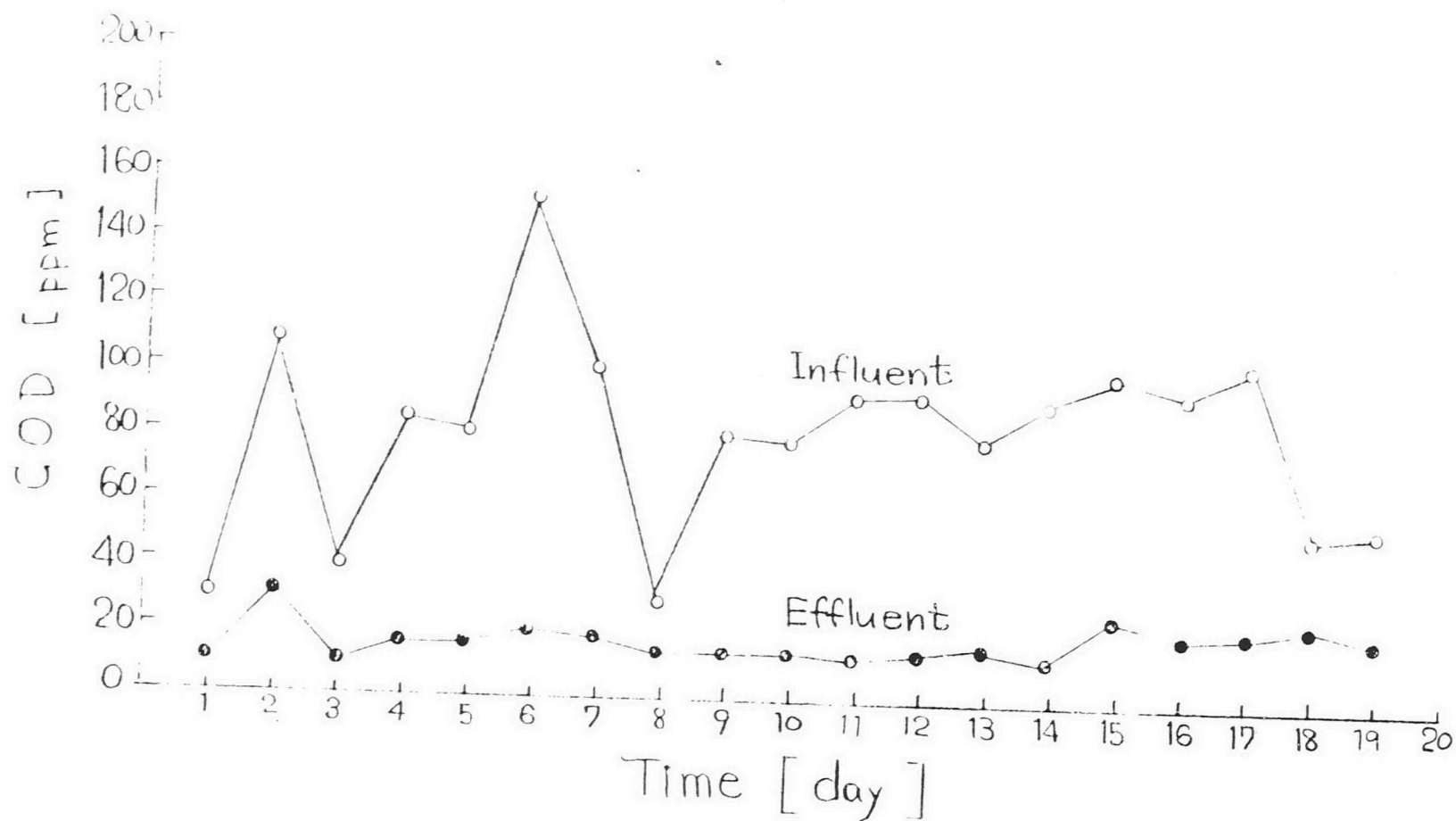
Fig. 2-21   Influent and Effluent COD

Fig. 2-22 Correlation between treatment efficiency and F/M
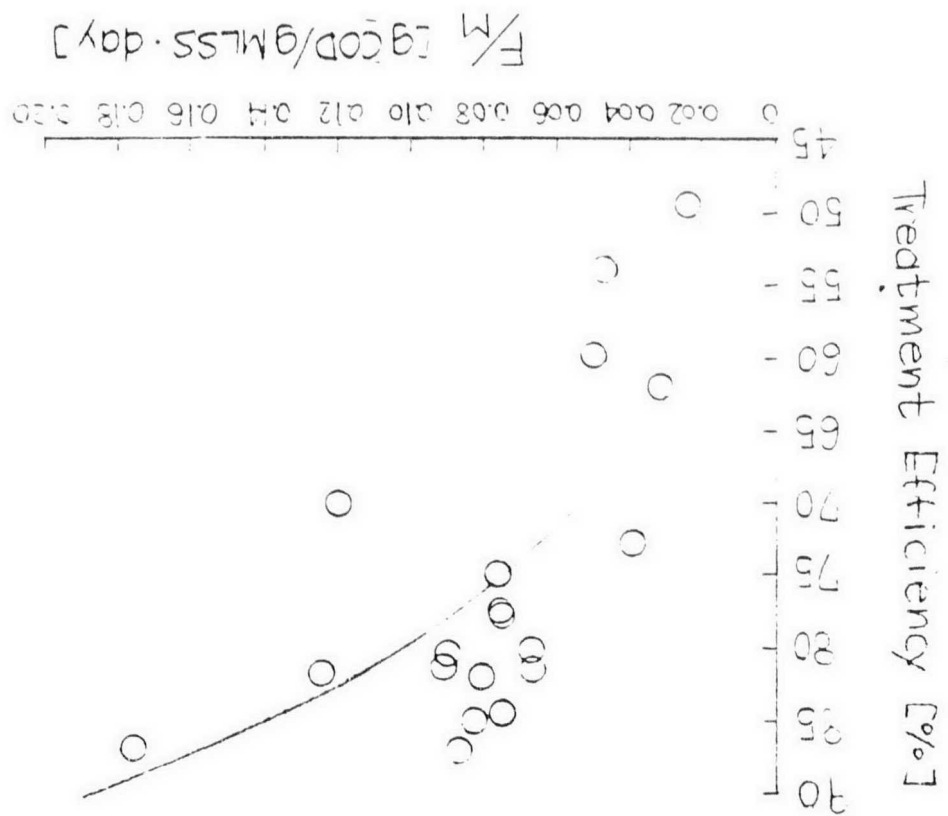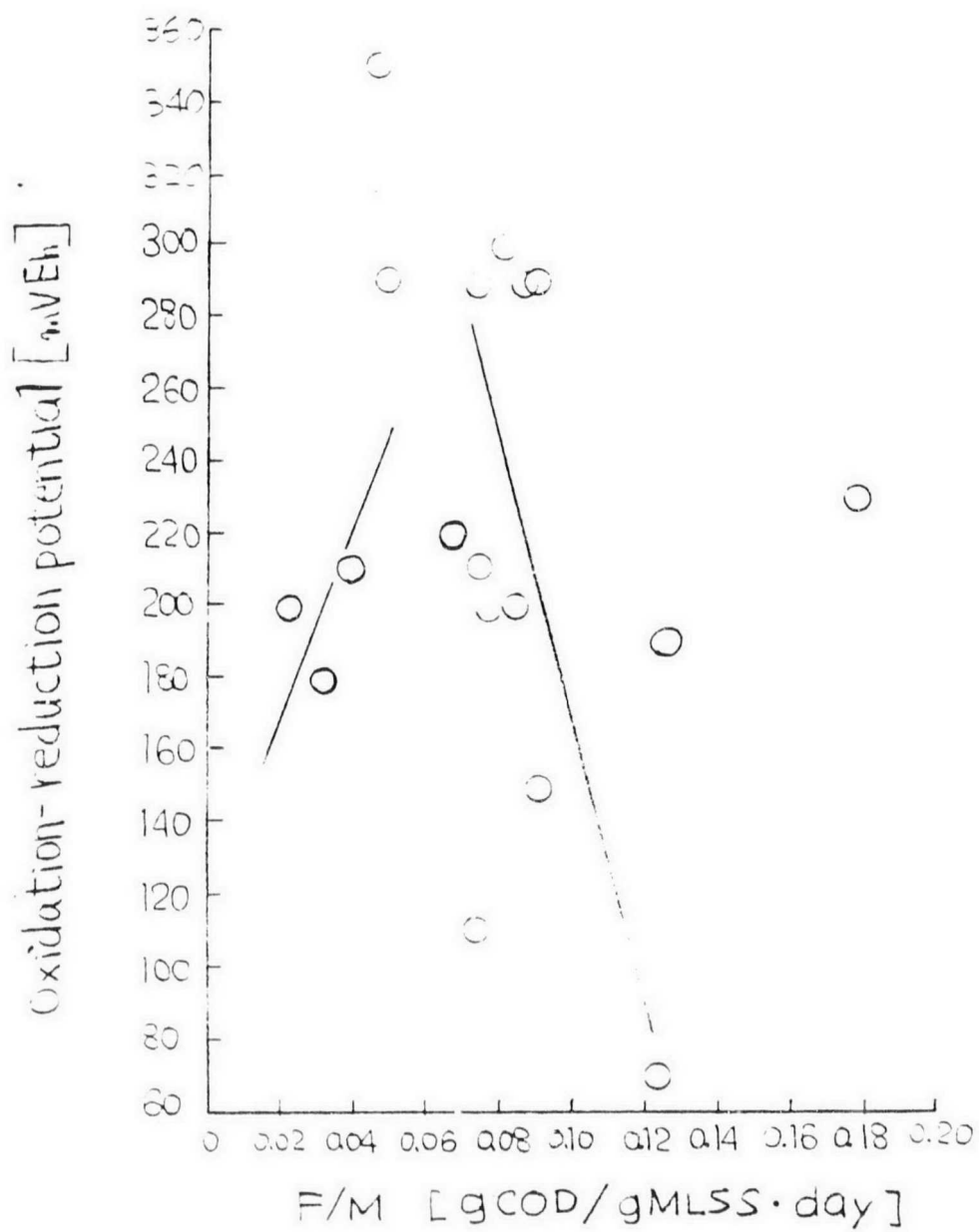
Fig. 2-23 Correlation between O.R.P. and F/M
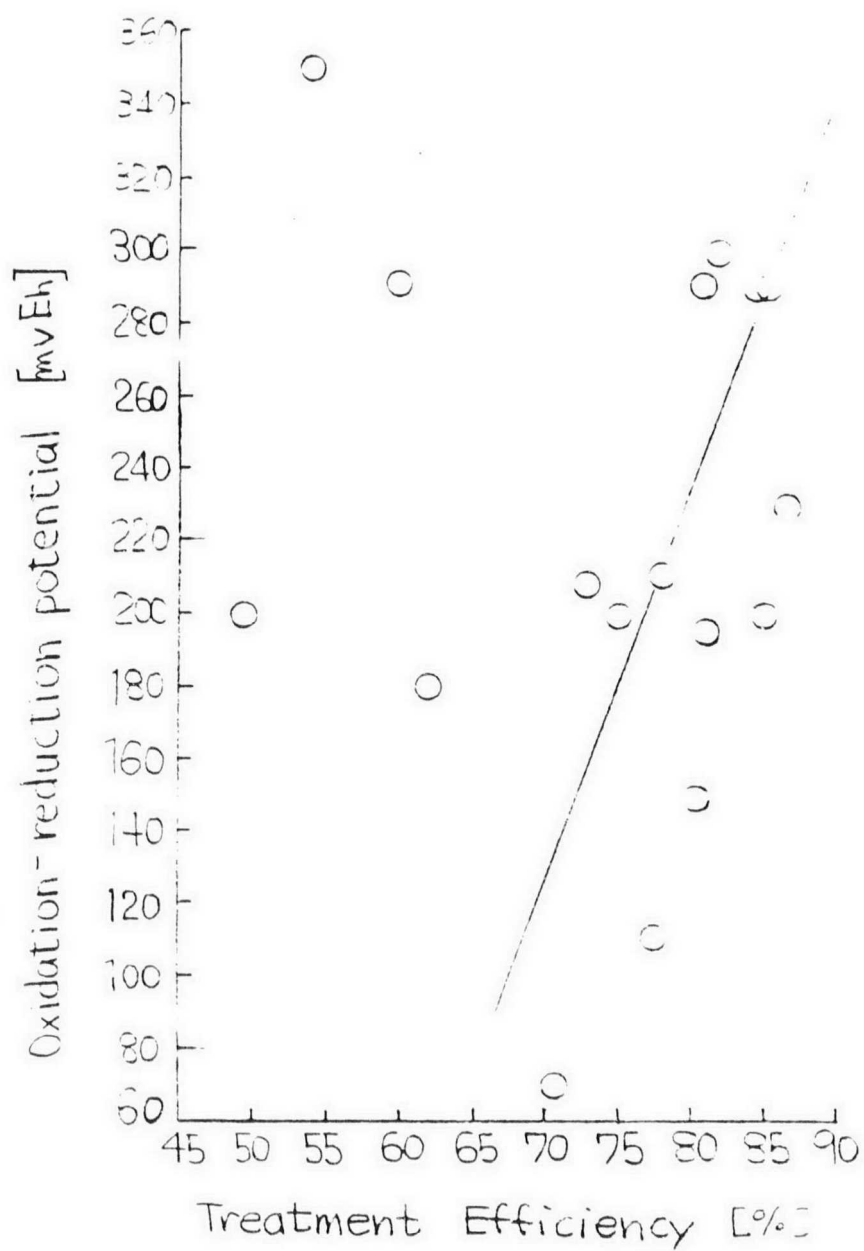
Fig. 2-24 Correlation between O.R.F. and treatment efficiency
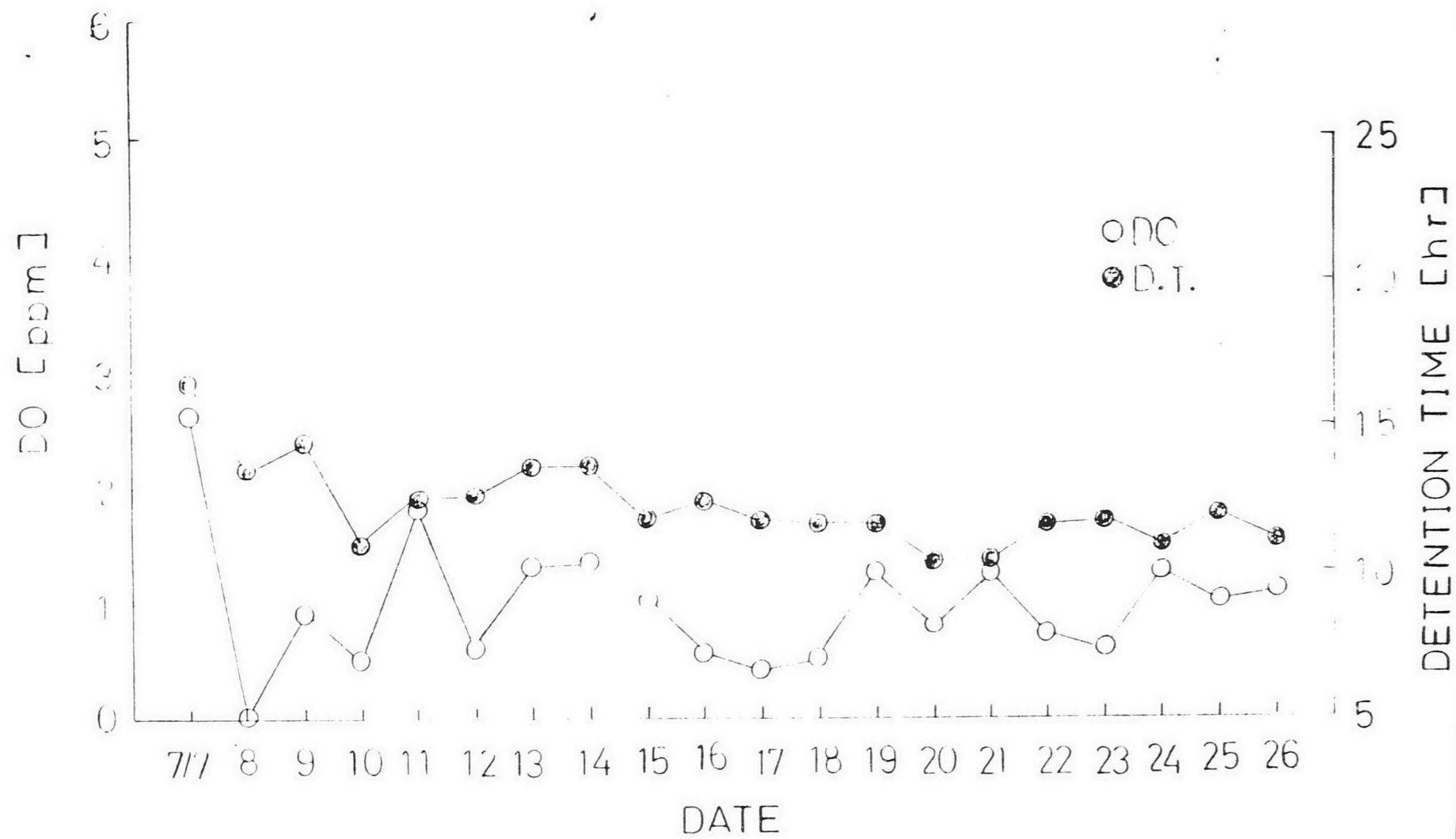
Fig 2.25   DO & DETENTION TIME I (7/7 ~ 7/26)
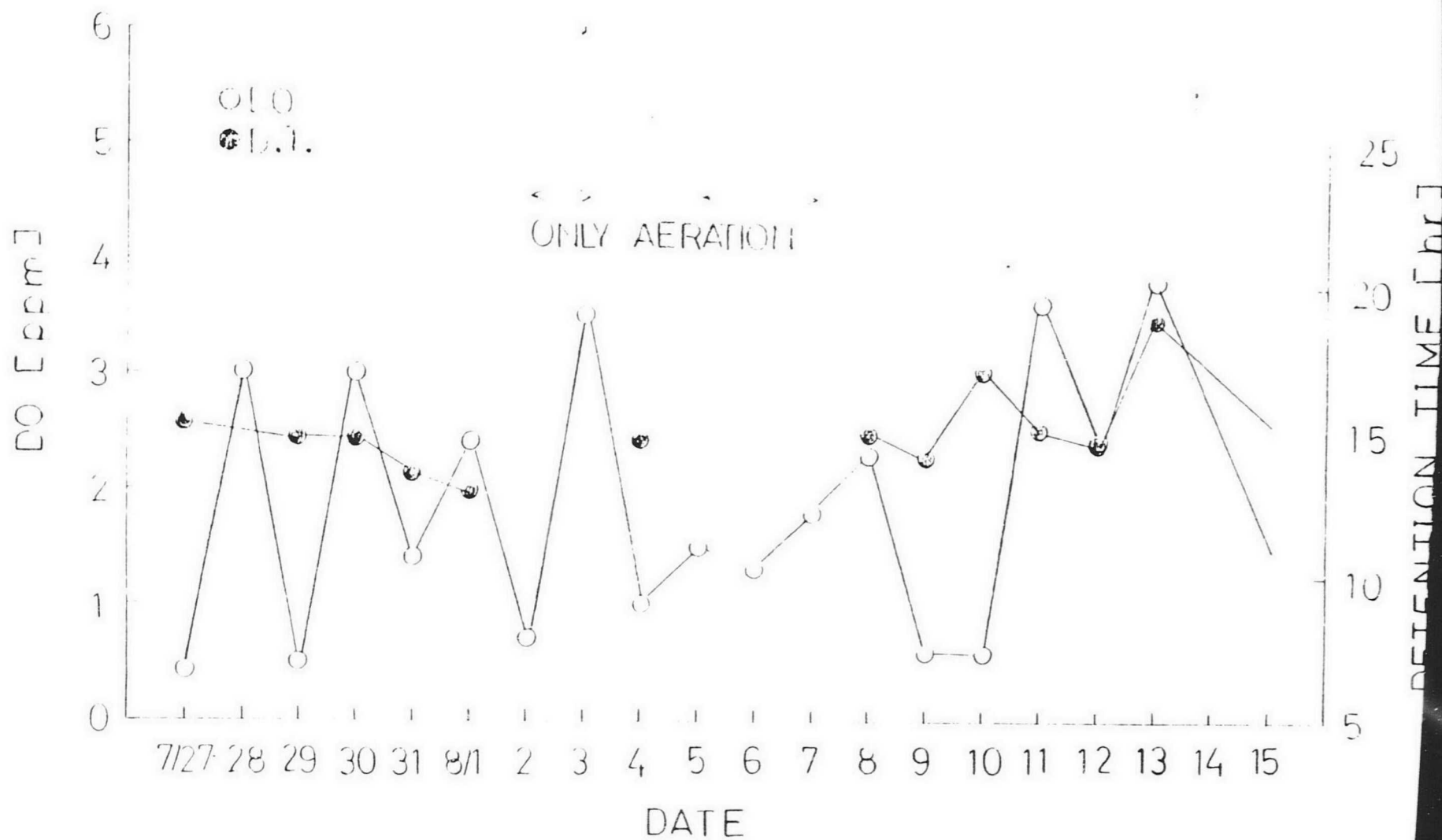
Fig 2.26   DO & DETENTION TIME   II (7/27~8/15)
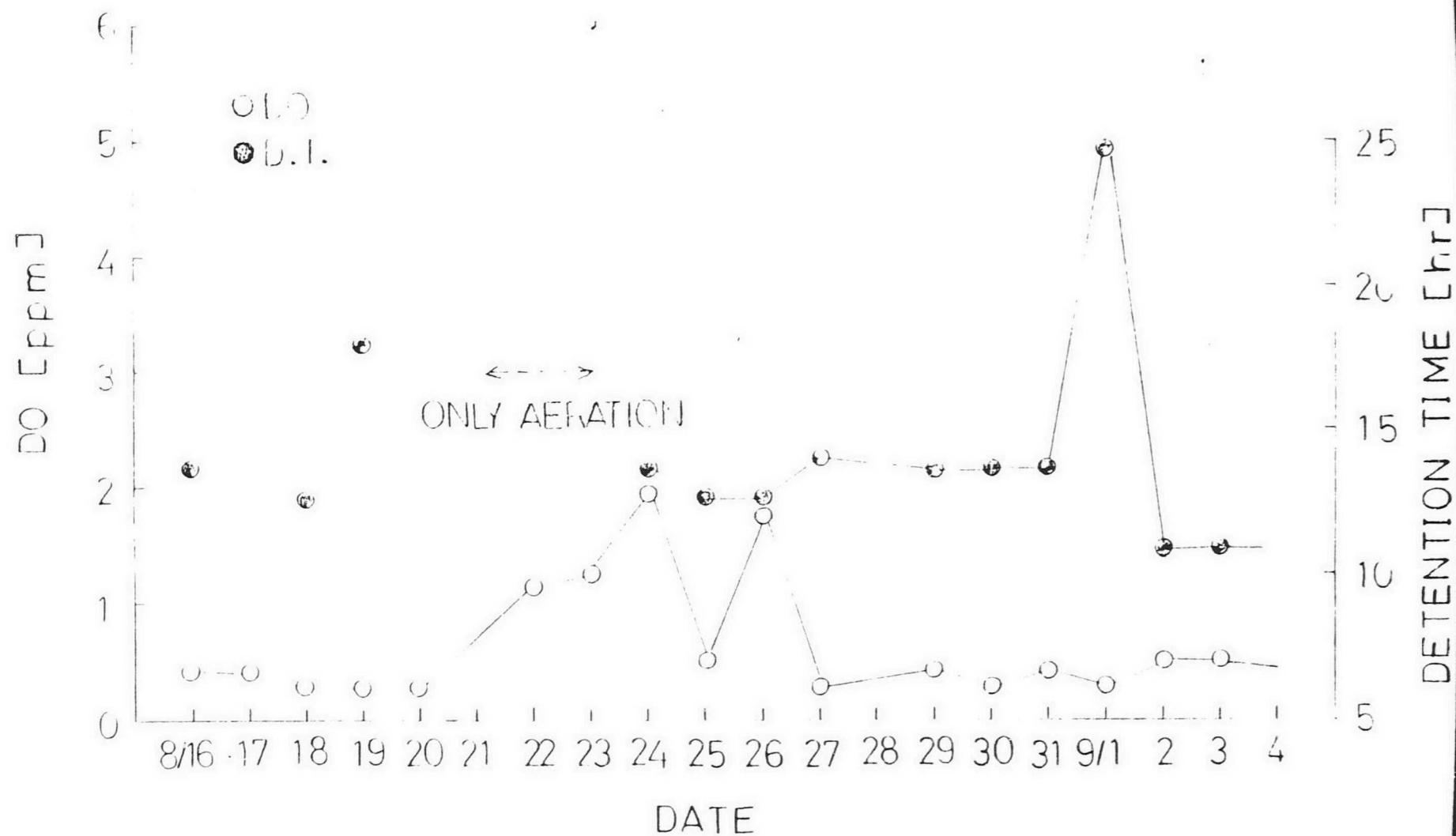
Fig. 2.27   DO & DETENTION TIME   III (8/16 ~ 9/4)
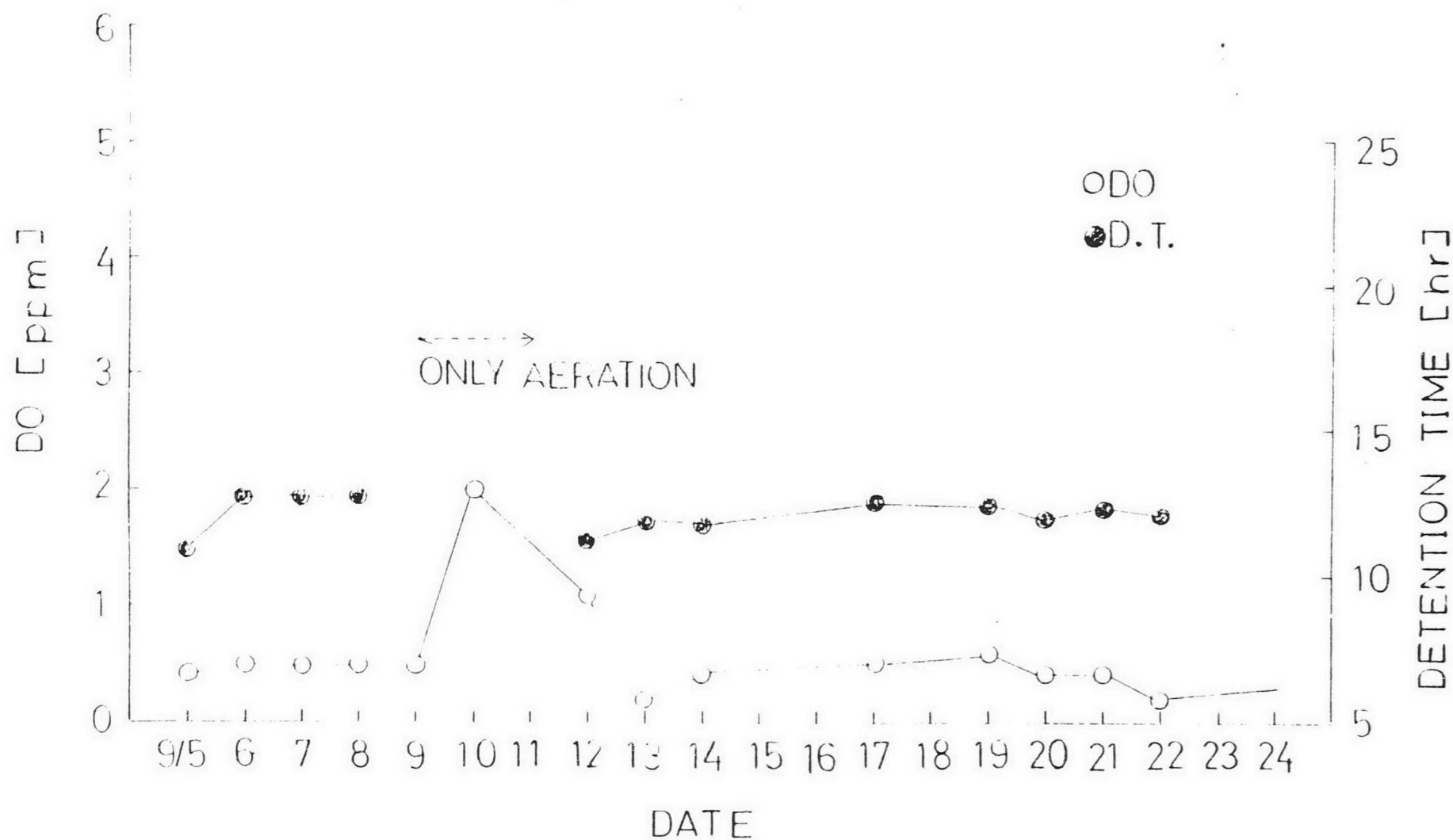
Fig. 2.28   DO & DETENTION TIME   IV   (9/5~9/24)
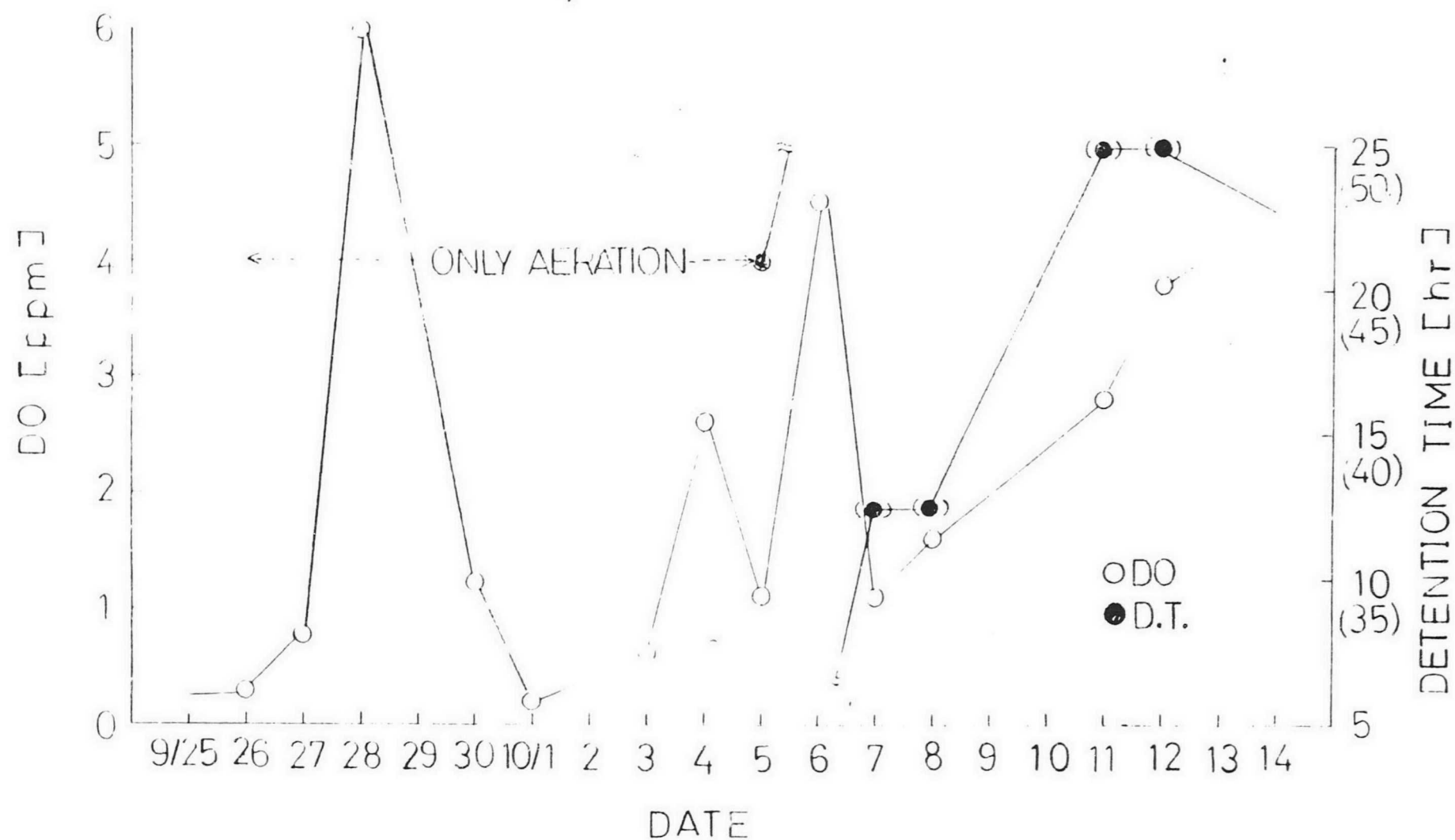
Fig. 2.29   DO & DETENTION TIME   V   (9/25 ~ 10/14)
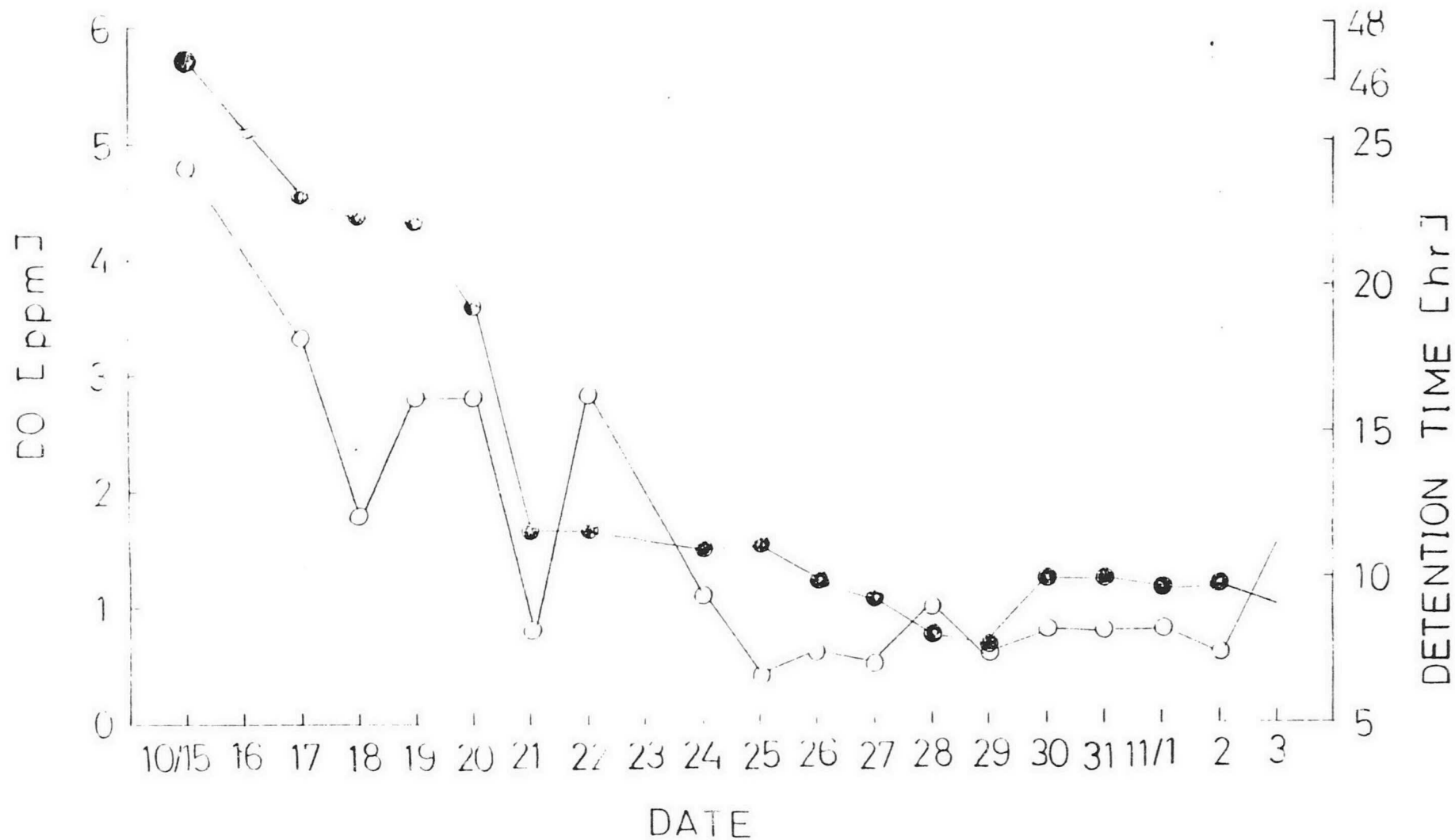
.2.30 DO & DETENTION TIME VI (10/15 ~ 11/3)
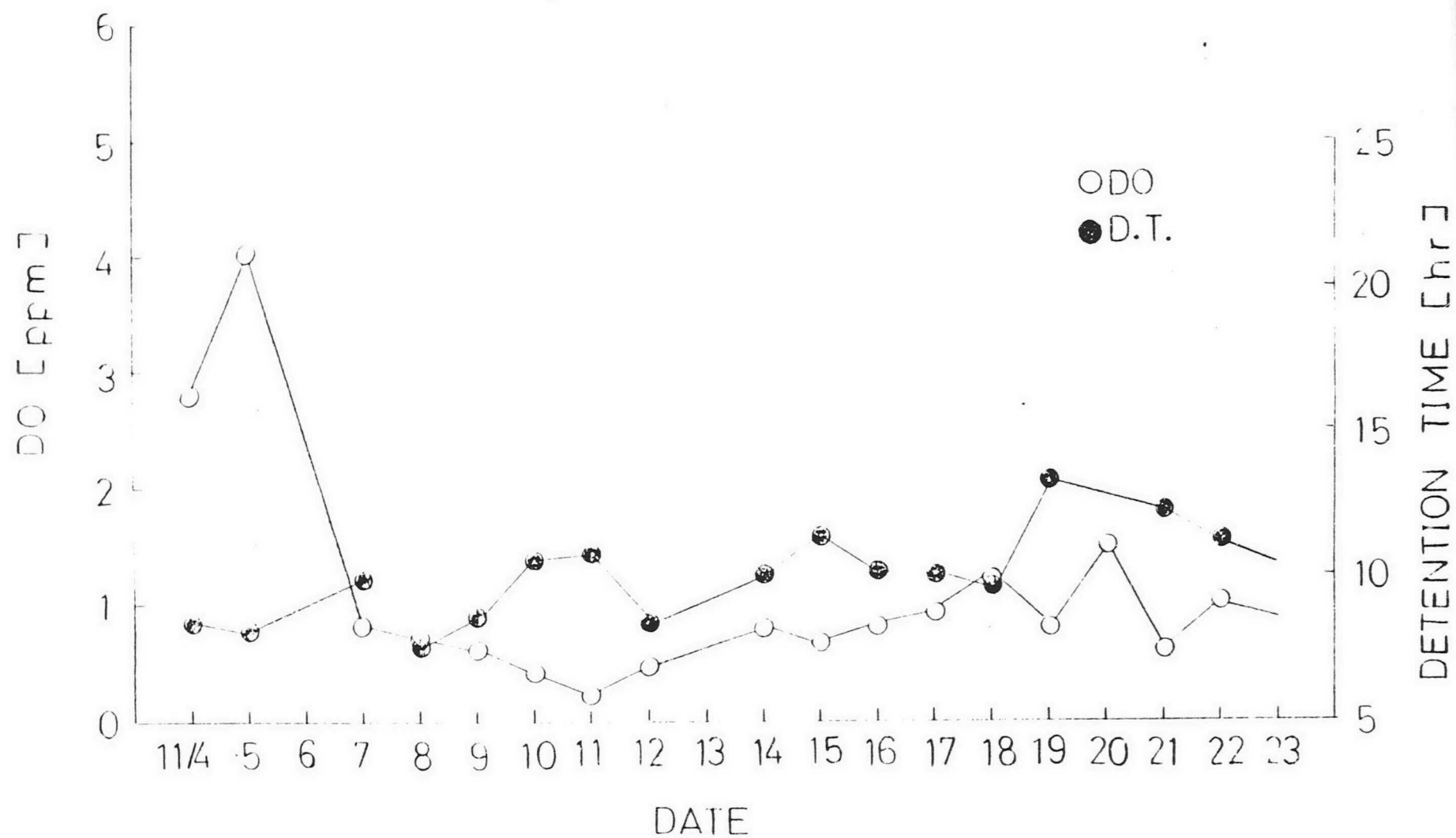
Fig. 2.31   DO & DETENTION TIME   VII   (11/4~11/23)
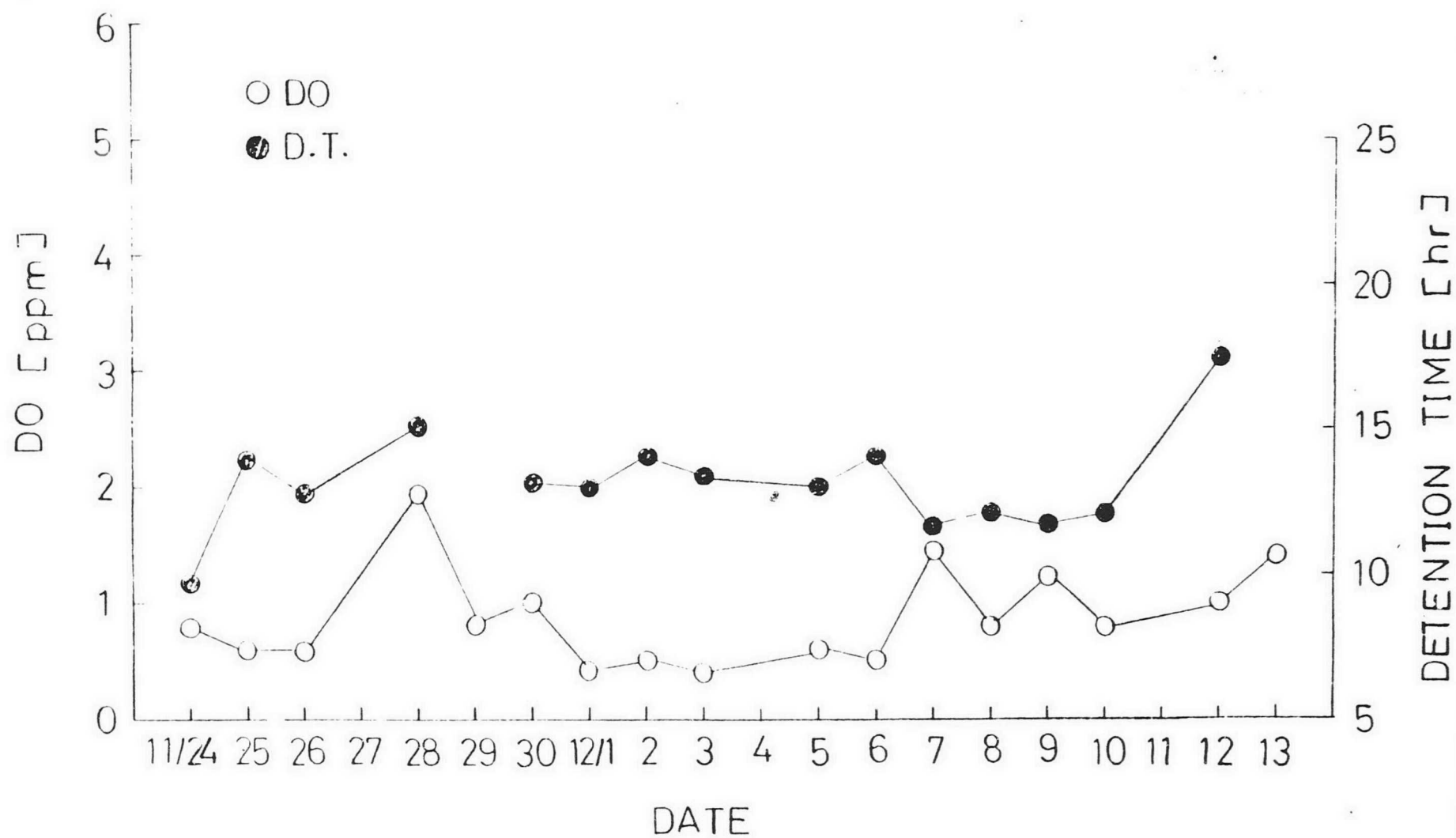
Fig. 2.32   DO & DETENTION TIME   VIII   (11/24 ~ 12/13)
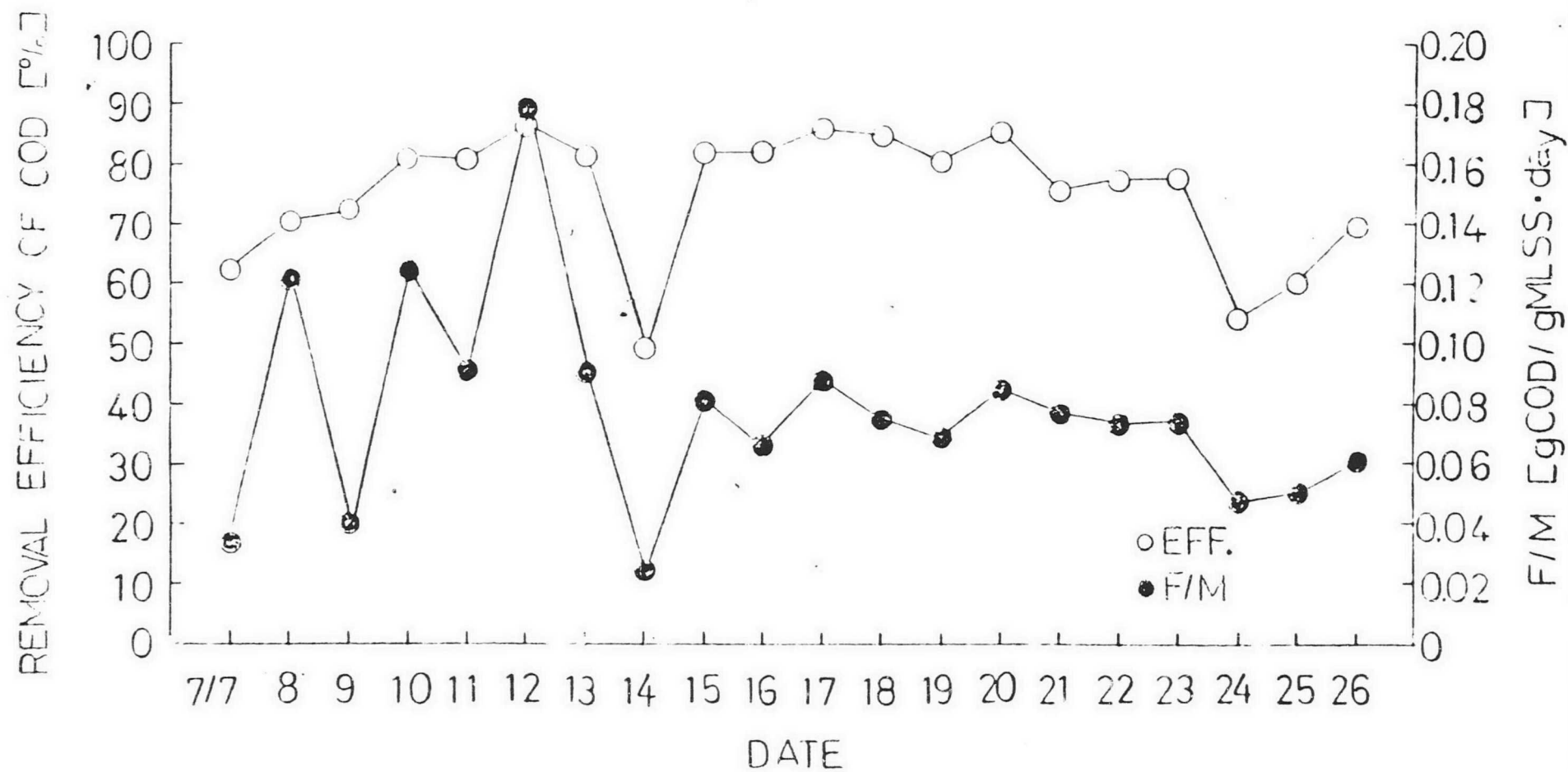
Fig 2.33   REMOVAL EFICIENCY OF COD & F/M I (7/7 ~ 7/26)
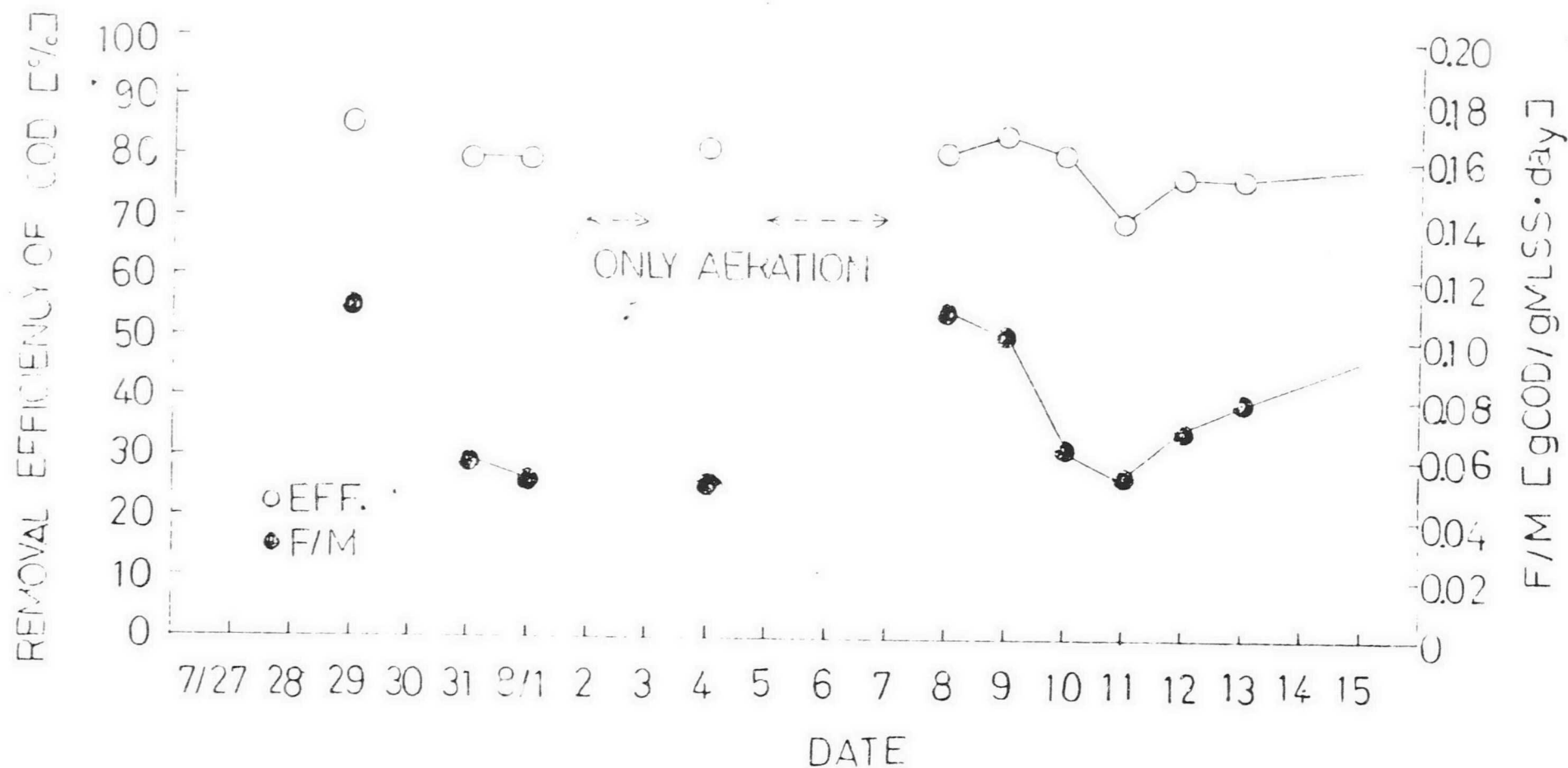
Fig. 2.34   REMOVAL EFICIENCY OF COD & F/M   II   (7/27∼8/15)
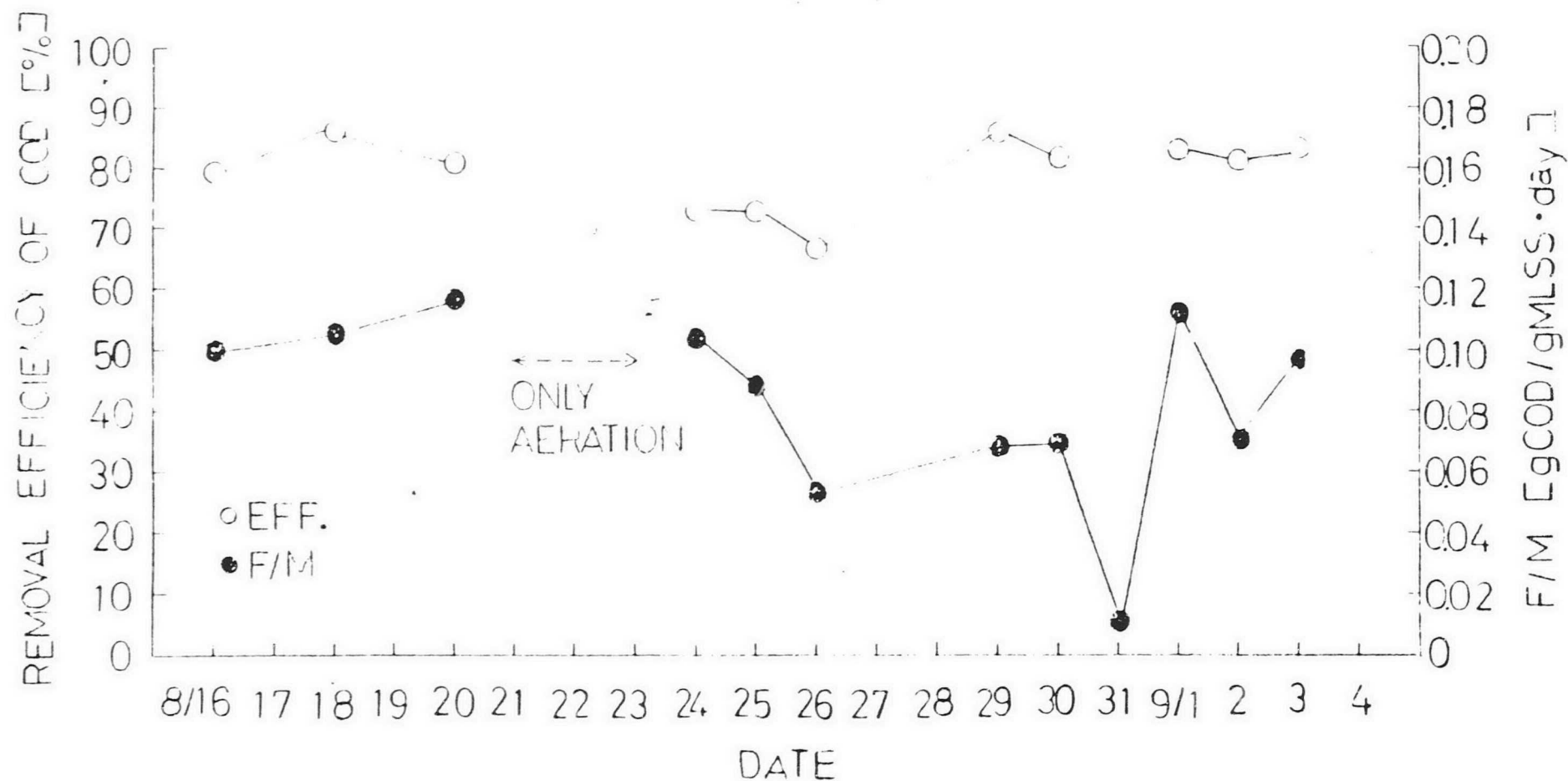
Fig.2·35   REMOVAL EFICIENCY OF COD & F/M III (8/16～9/4)
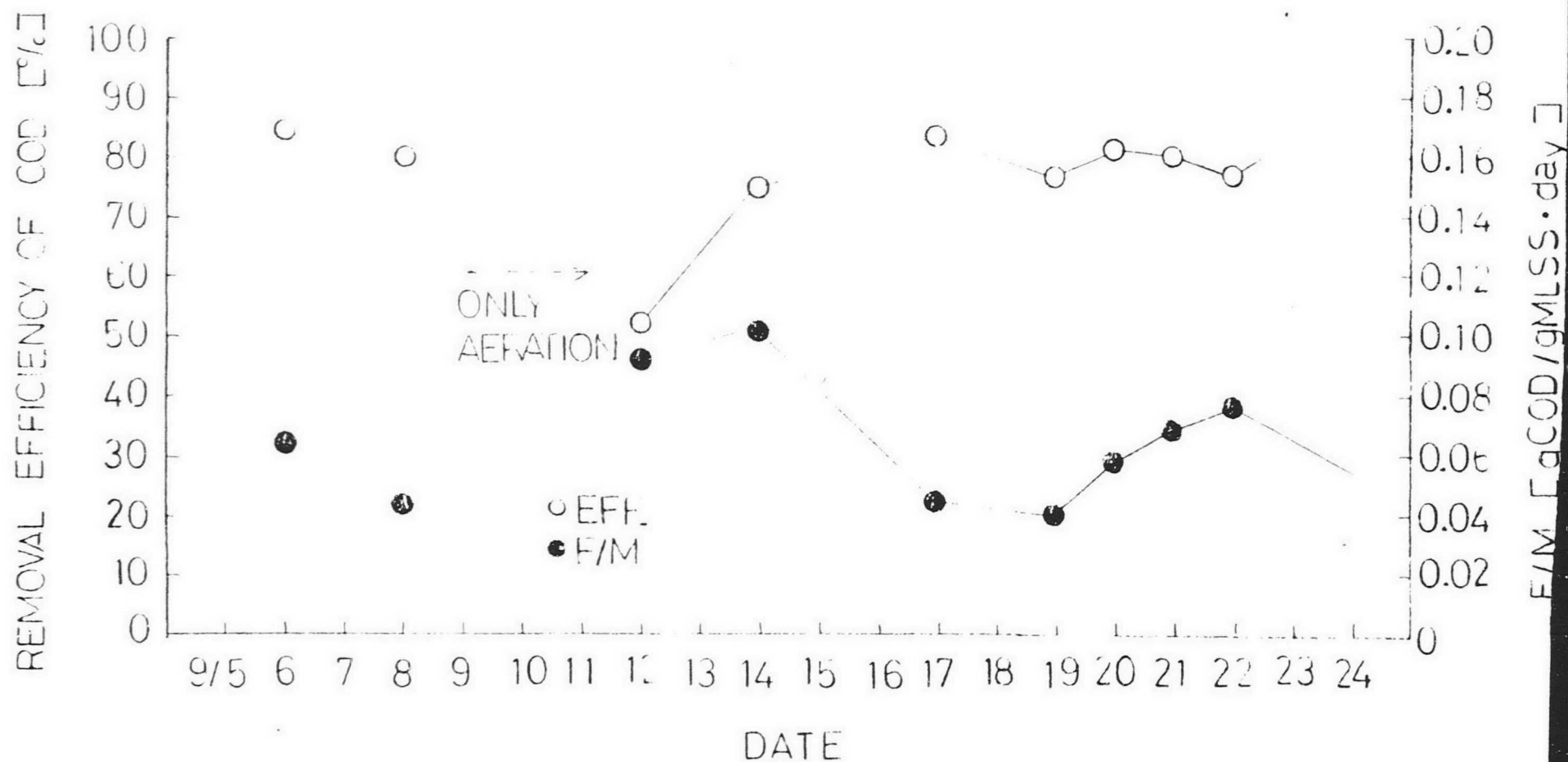
Fig. 2.36   REMOVAL EFICIENCY OF COD & F/M   IV   (9/5 ~ 9/24)
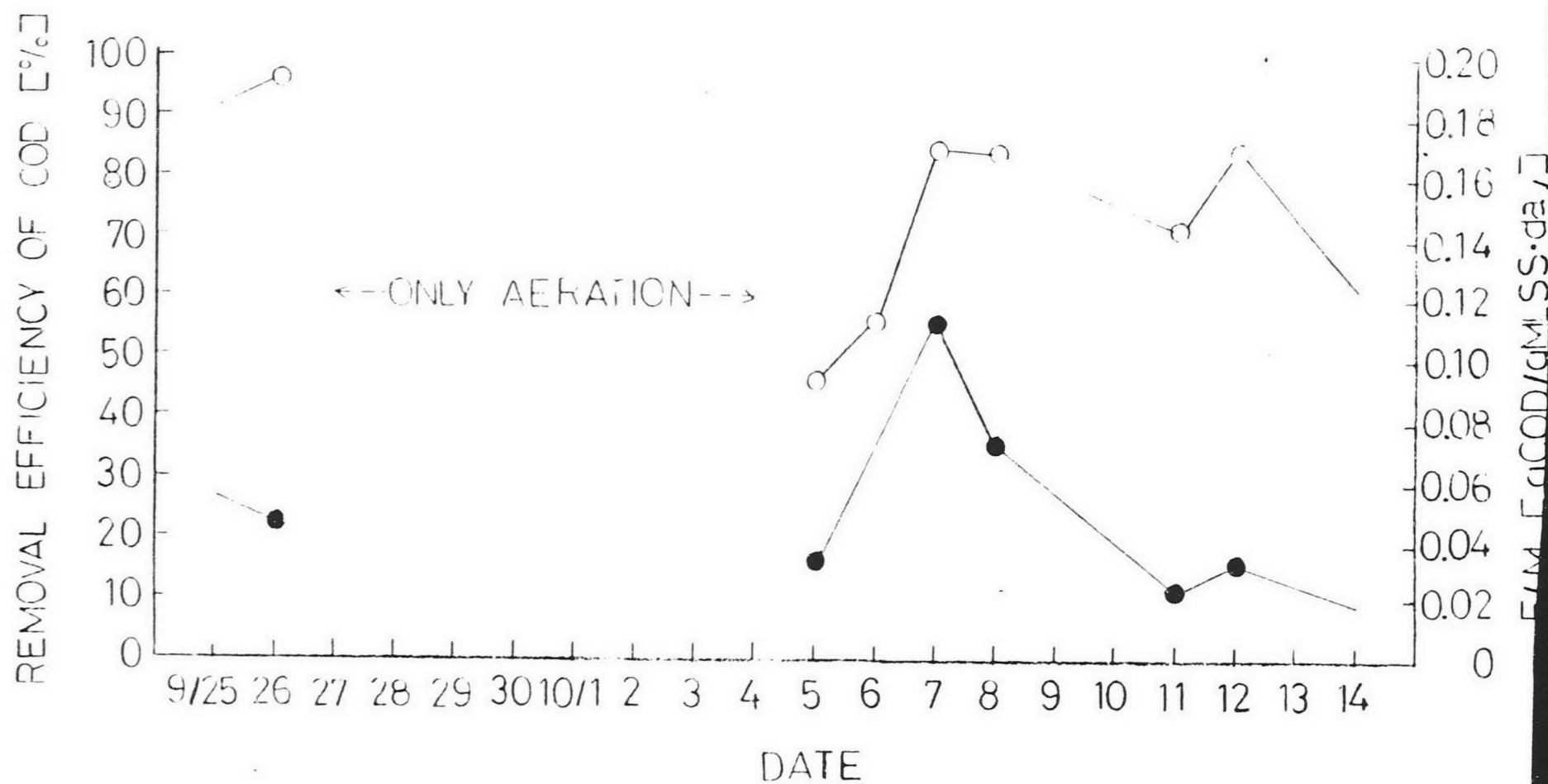
Fig. 2.37　REMOVAL EFFICIENCY OF COD & F/M　V　(9/25～10/14)
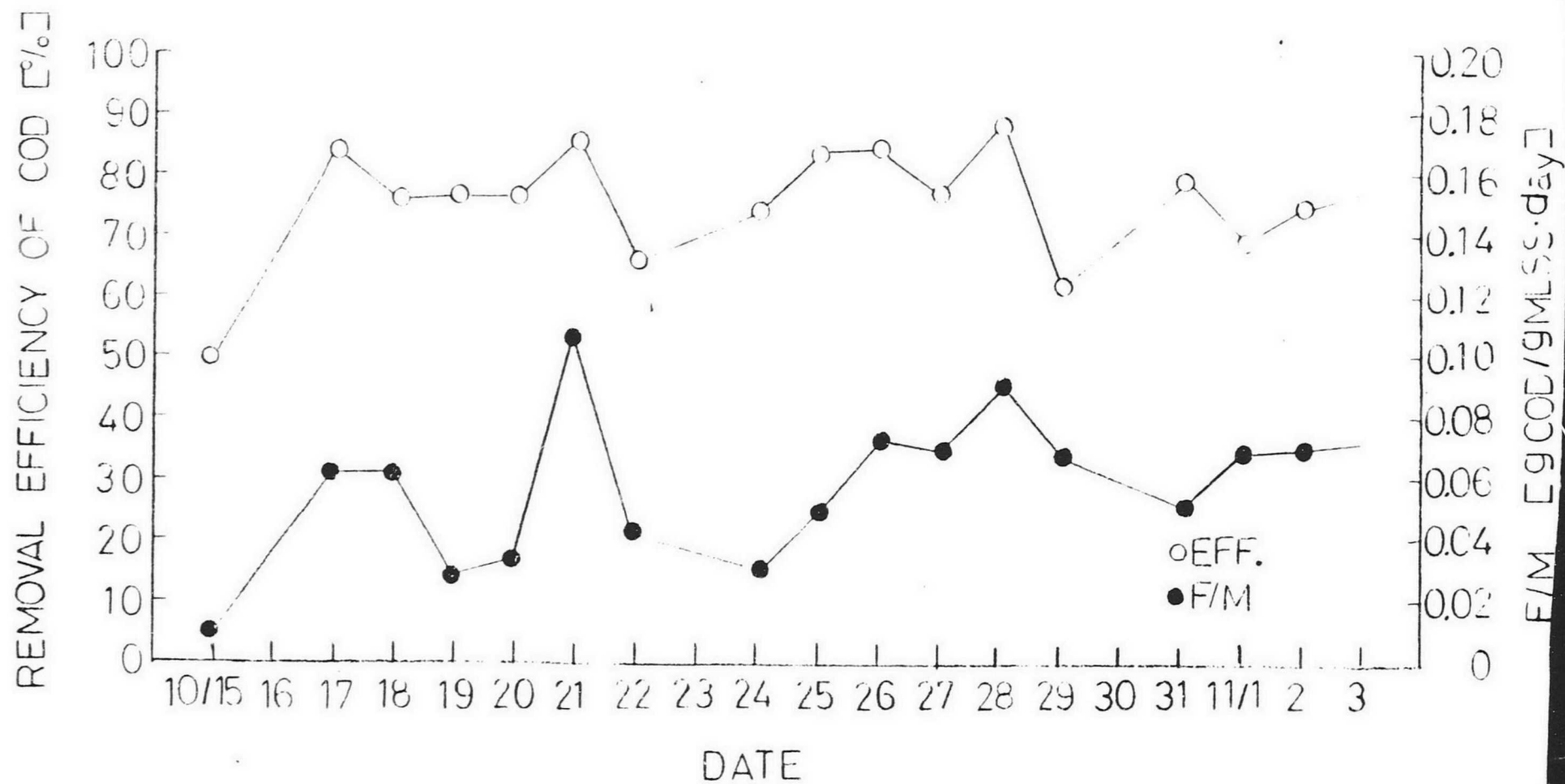
Fig. 2.38   REMOVAL EFICIENCY OF COD & F/M VI (10/15~11/3)
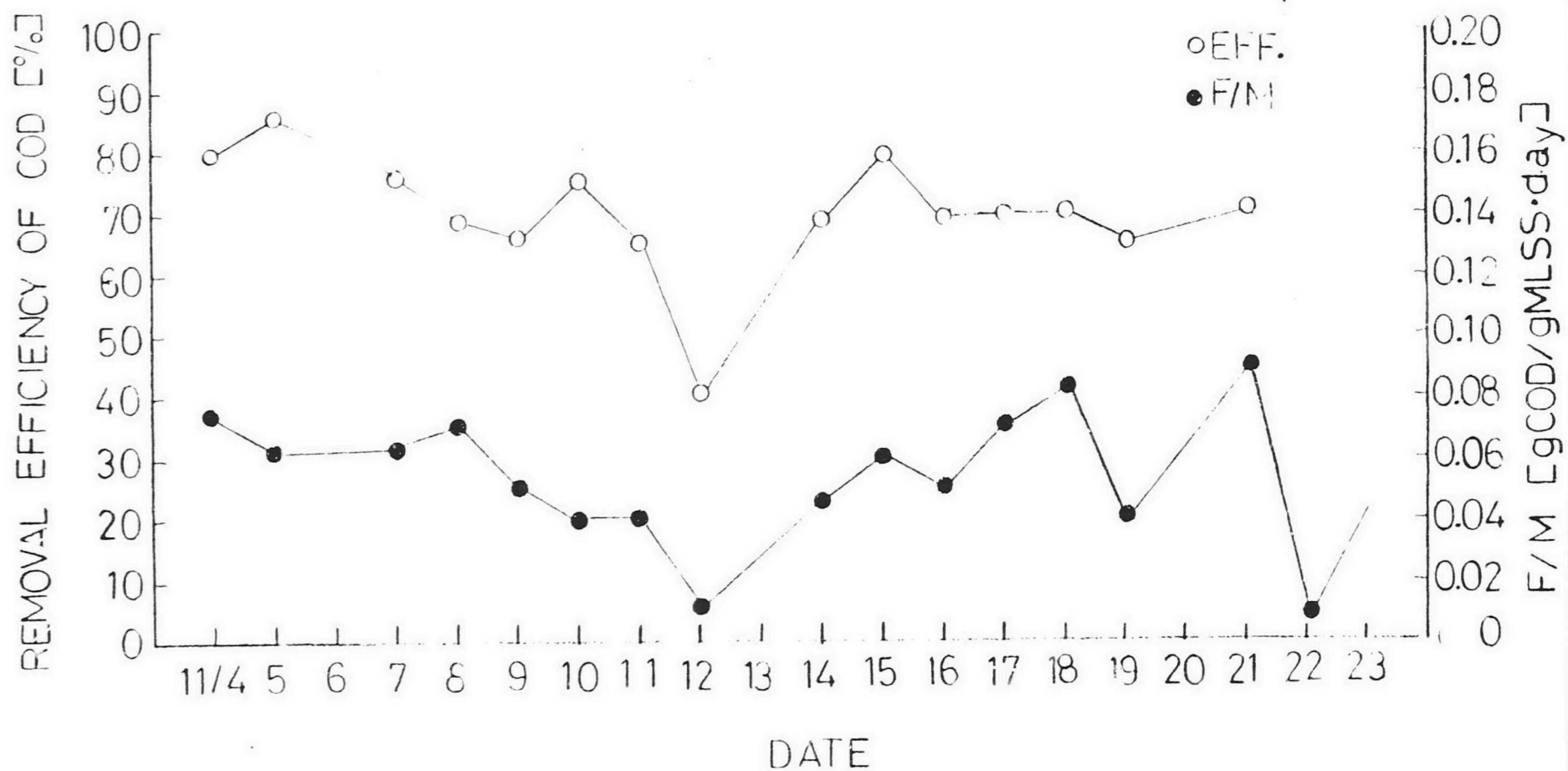
Fig. 2. 39   REMOVAL EFFICIENCY OF COD & F/M   VII   (11/4 ~ 11/23)
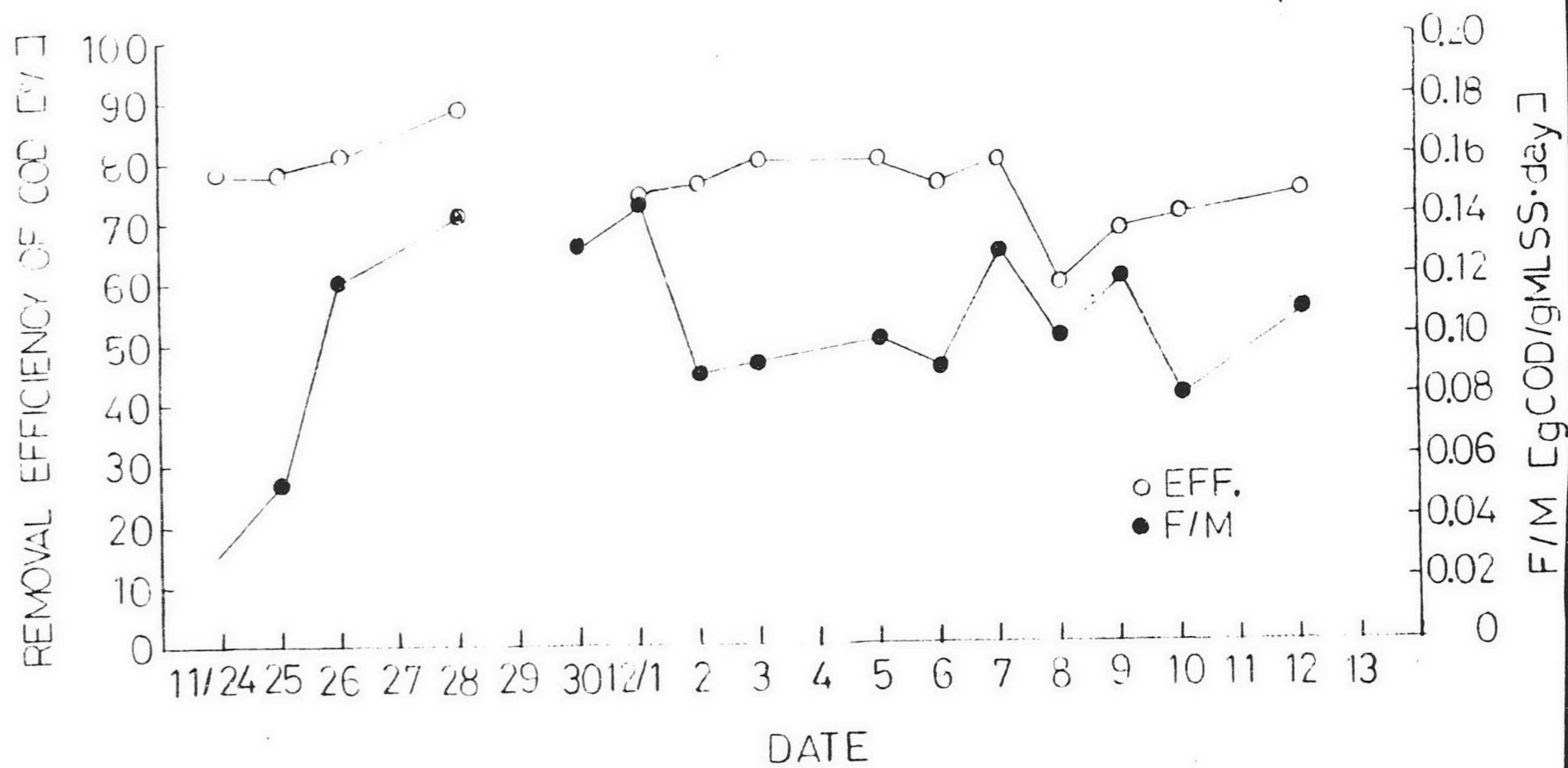
Fig 2.40   REMOVAL EFICIENCY OF COD & F/M VIII (11/24~12/13)

Fig. 2.41   INFLUENT & EFFLUENT COD   I   (7/7～7/26)

INFLUENT & EFFLUENT COD
[ppm , mgO /l]

o IN
• EF

DATE

Fig.2.42   INFLUENT & EFFLUENT COD II (7/27~8/15)

INFLUENT & EFFLUENT COD
[ppm, mgO₂/l]
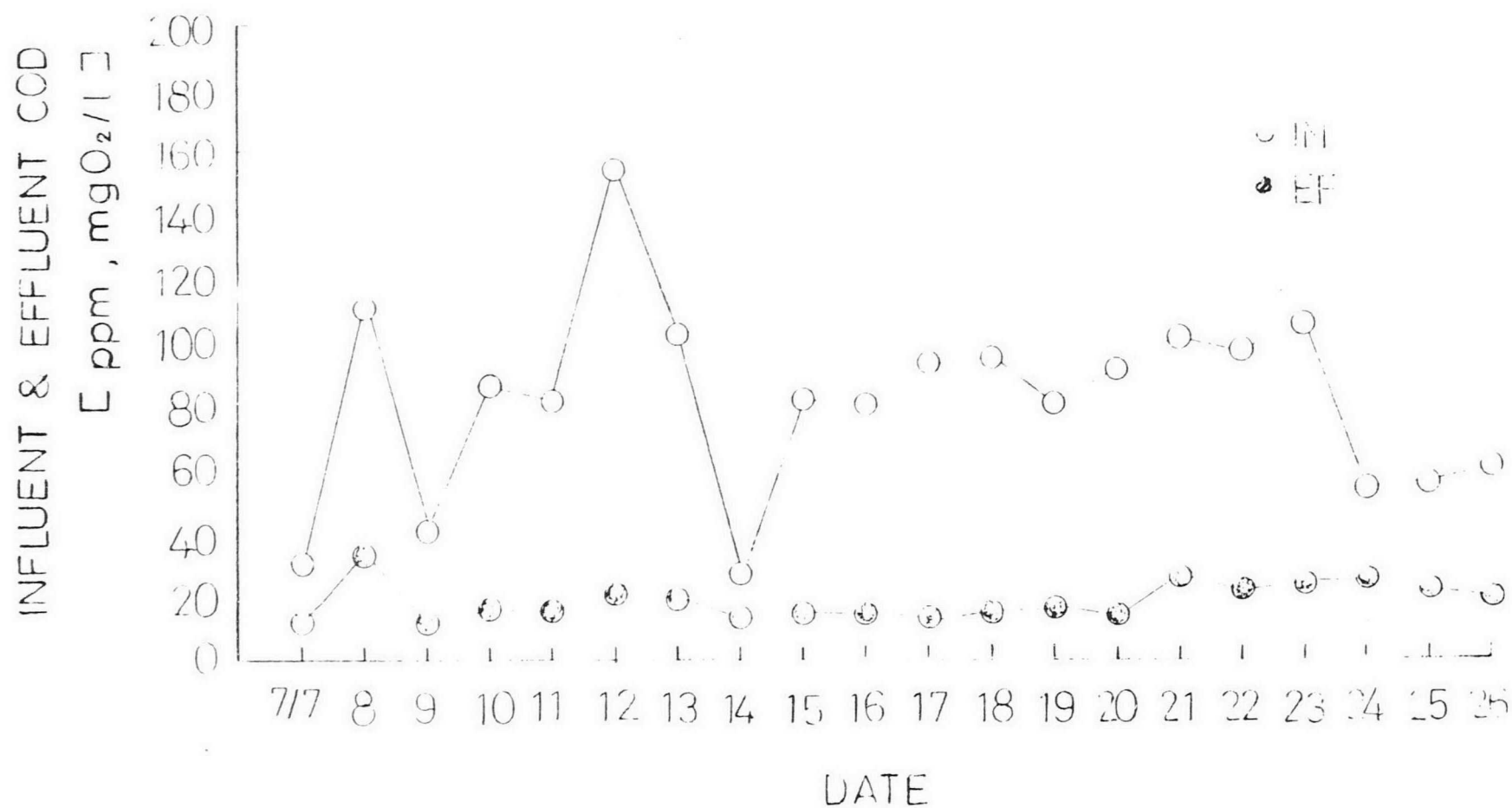
Fig 2.43   INFLUENT & EFFLUENT COD   III   (8/16 ~ 9/4)
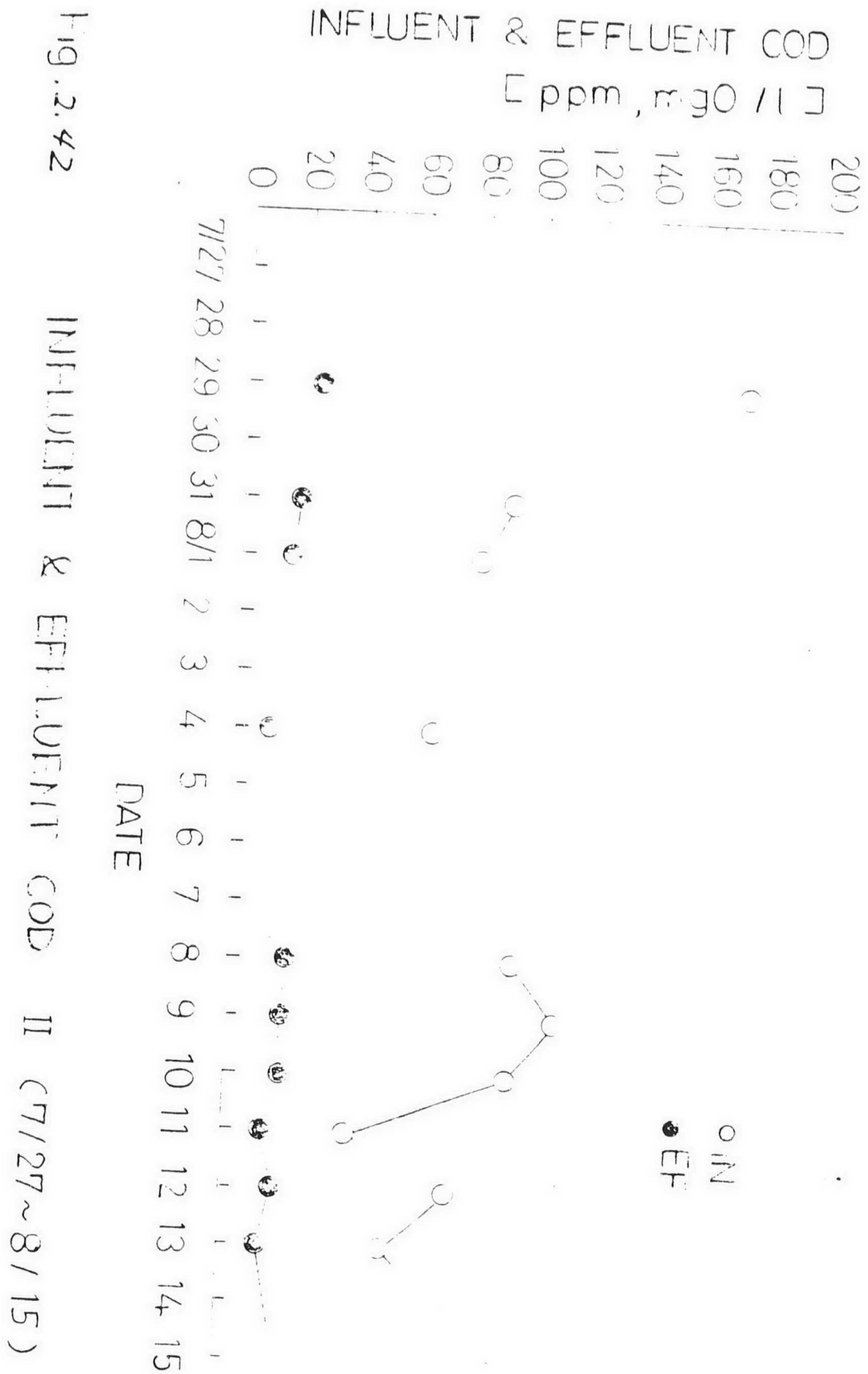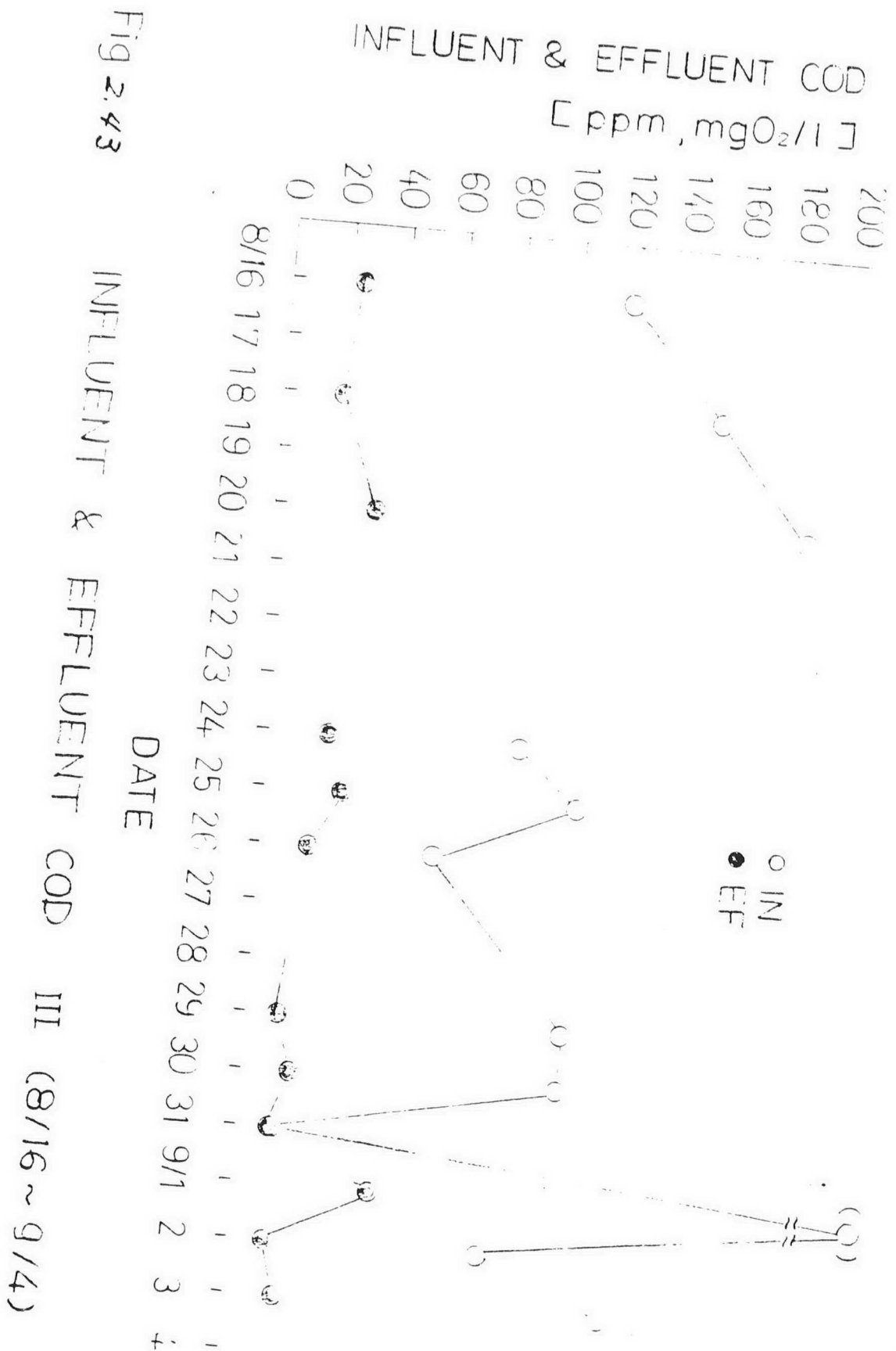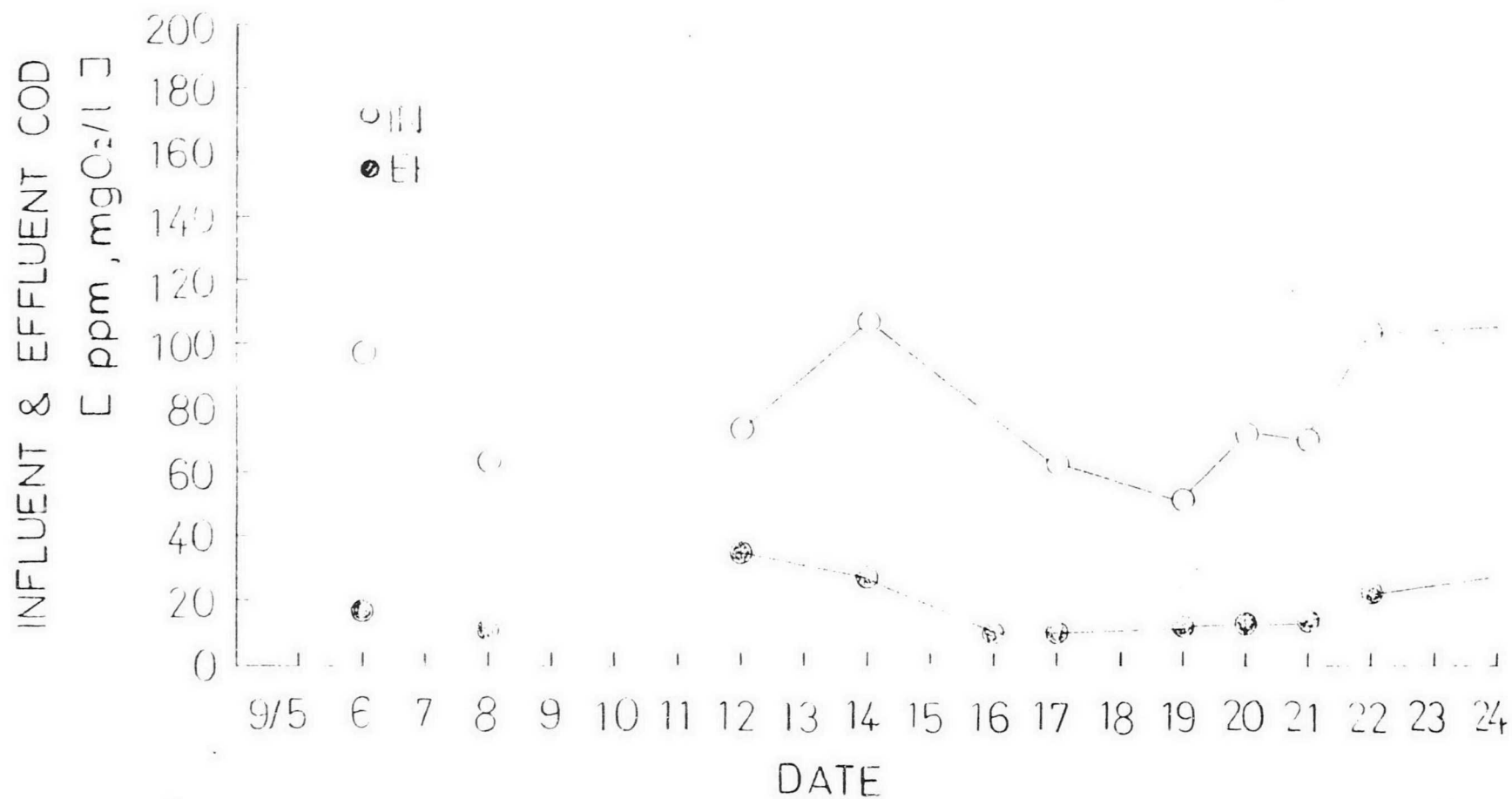
Fig. 2.44   INFLUENT & EFFLUENT COD   IV   (9/5 ~ 9/24)

INFLUENT & EFFLUENT COD [ppm , mgO₂/l]
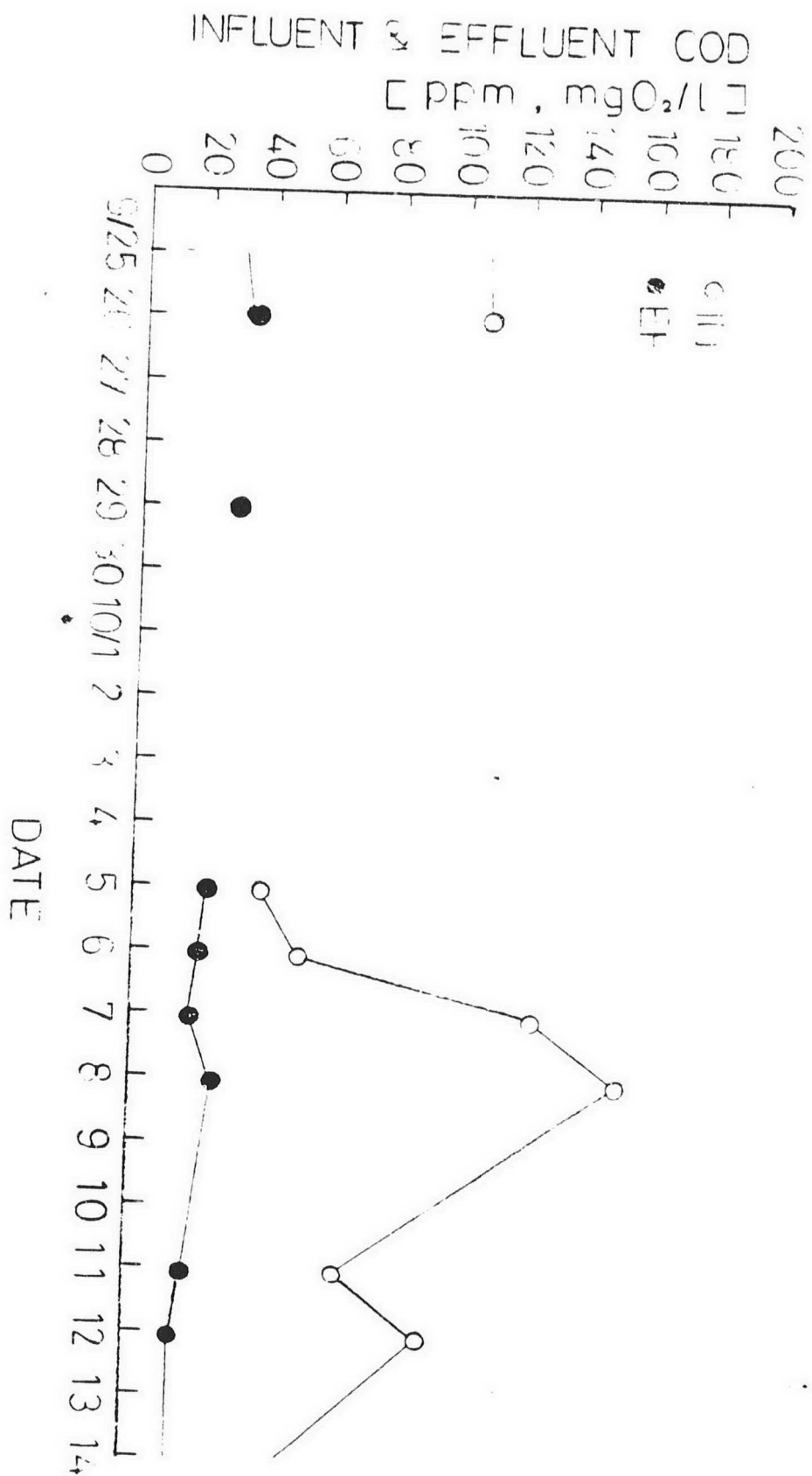
Fig. 2.45   INFLUENT & EFFLUENT COD V (9/25 ~ 10/14)
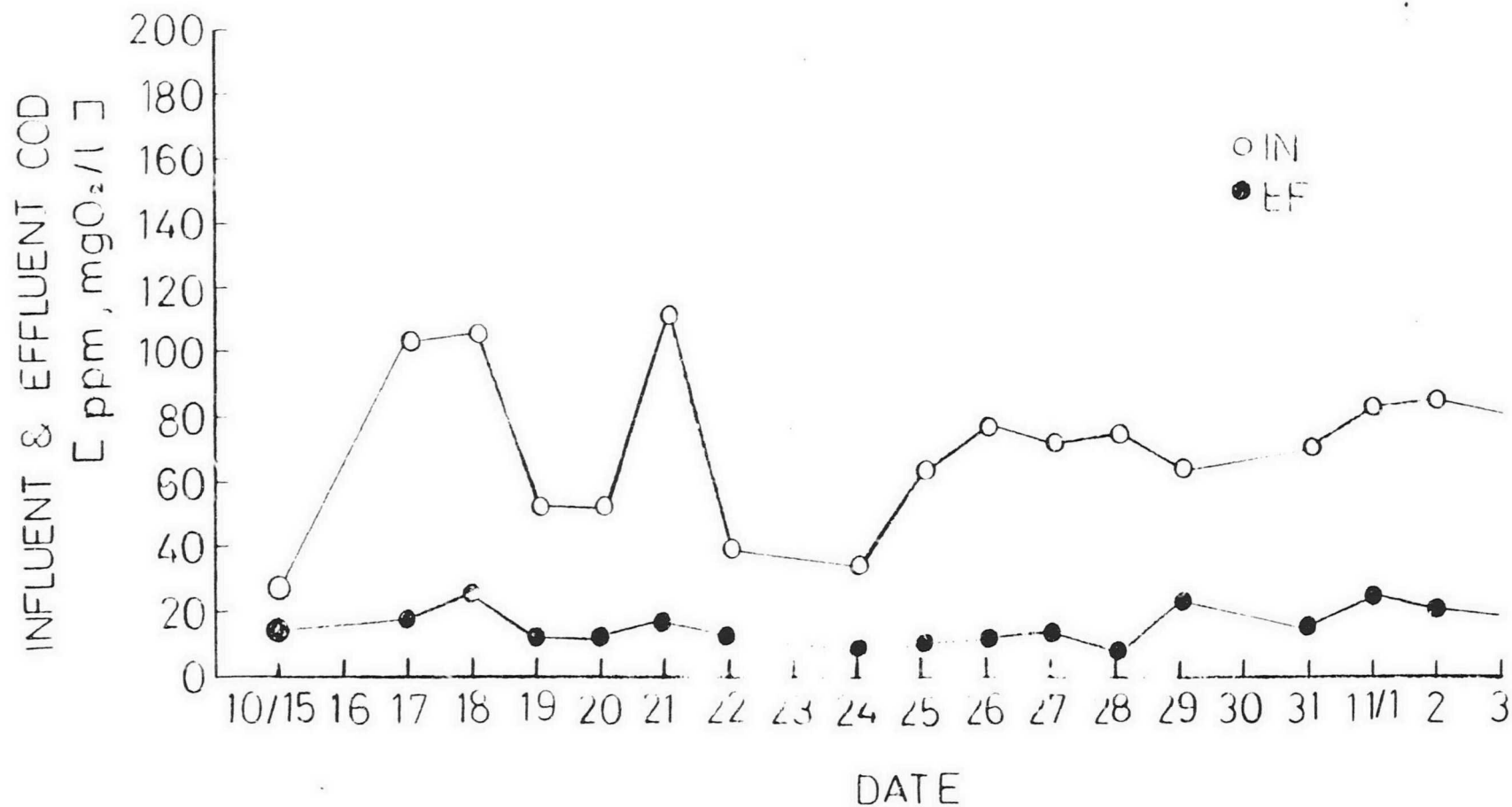
Fig.2.46   INFLUENT & EFFLUENT COD VI   (10/15 ~ 11/3)
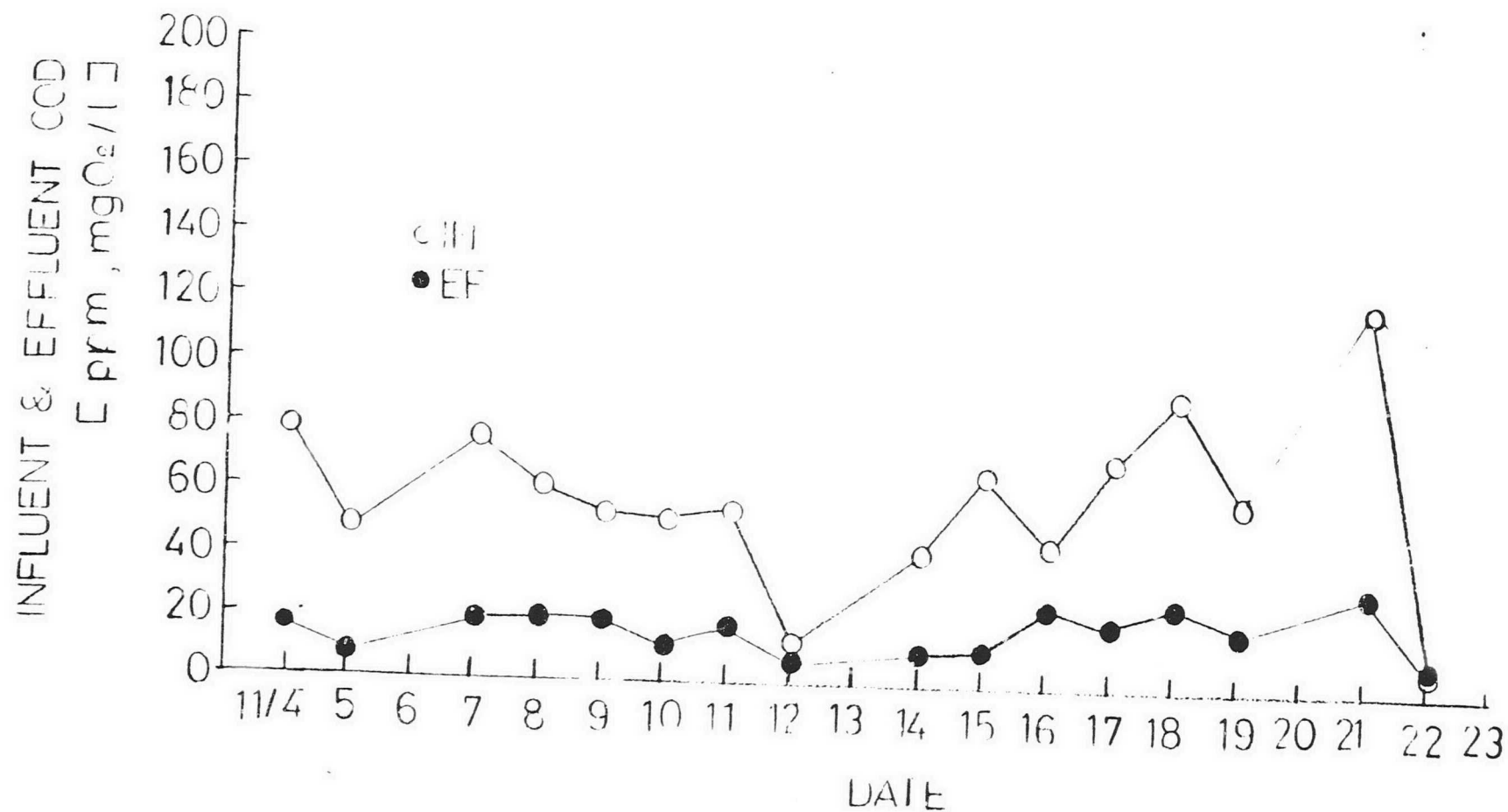
Fig. 2.47   INFLUENT & EFFLUENT COD   VII   (11/4 ~ 11/23)
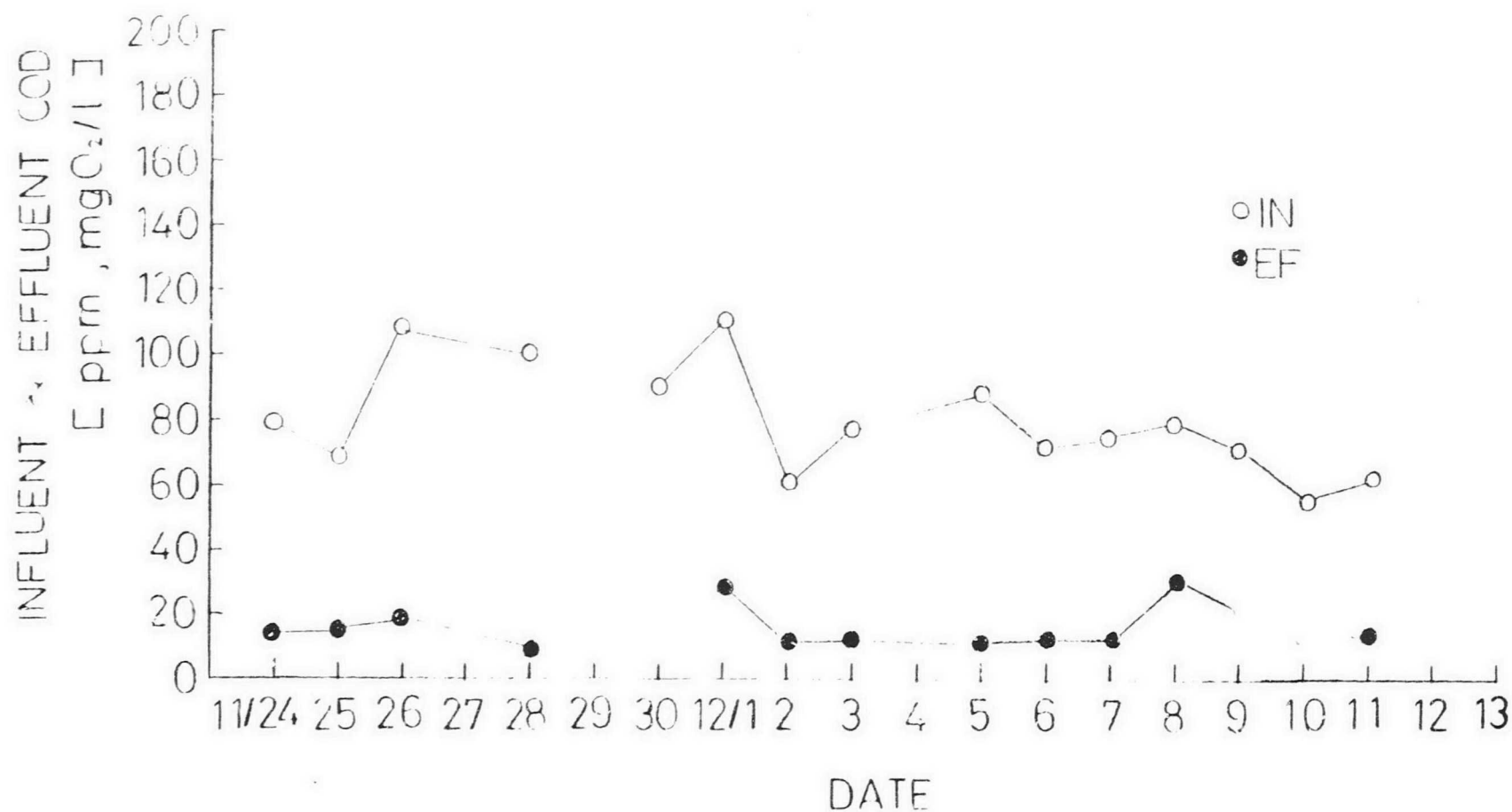
Fig. 2.48   INFLUENT & EFFLUENT COD   VIII   (11/24 ~ 12/13)
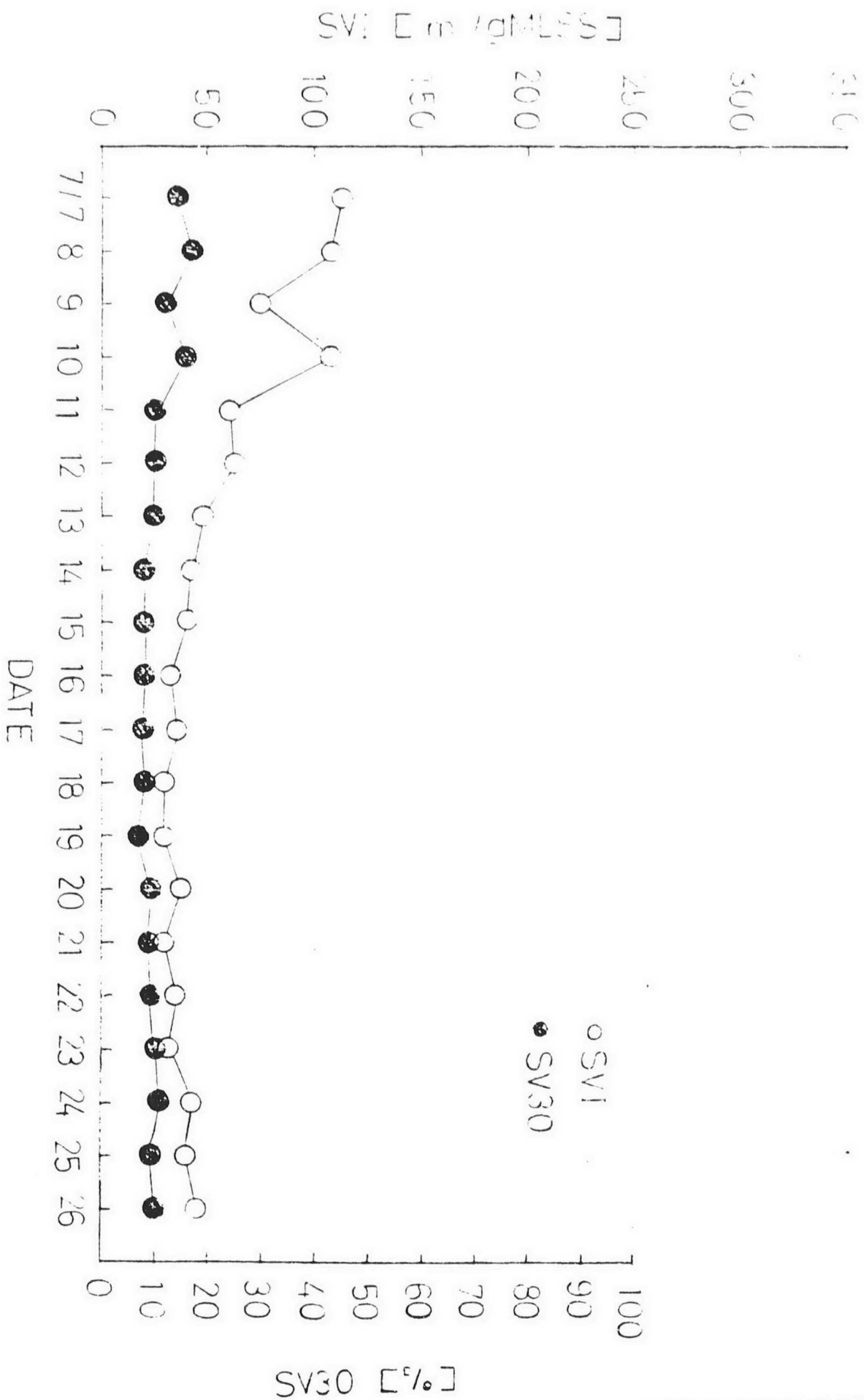
Fig.2.49. SVI & SV30 I (7/7～7/26)
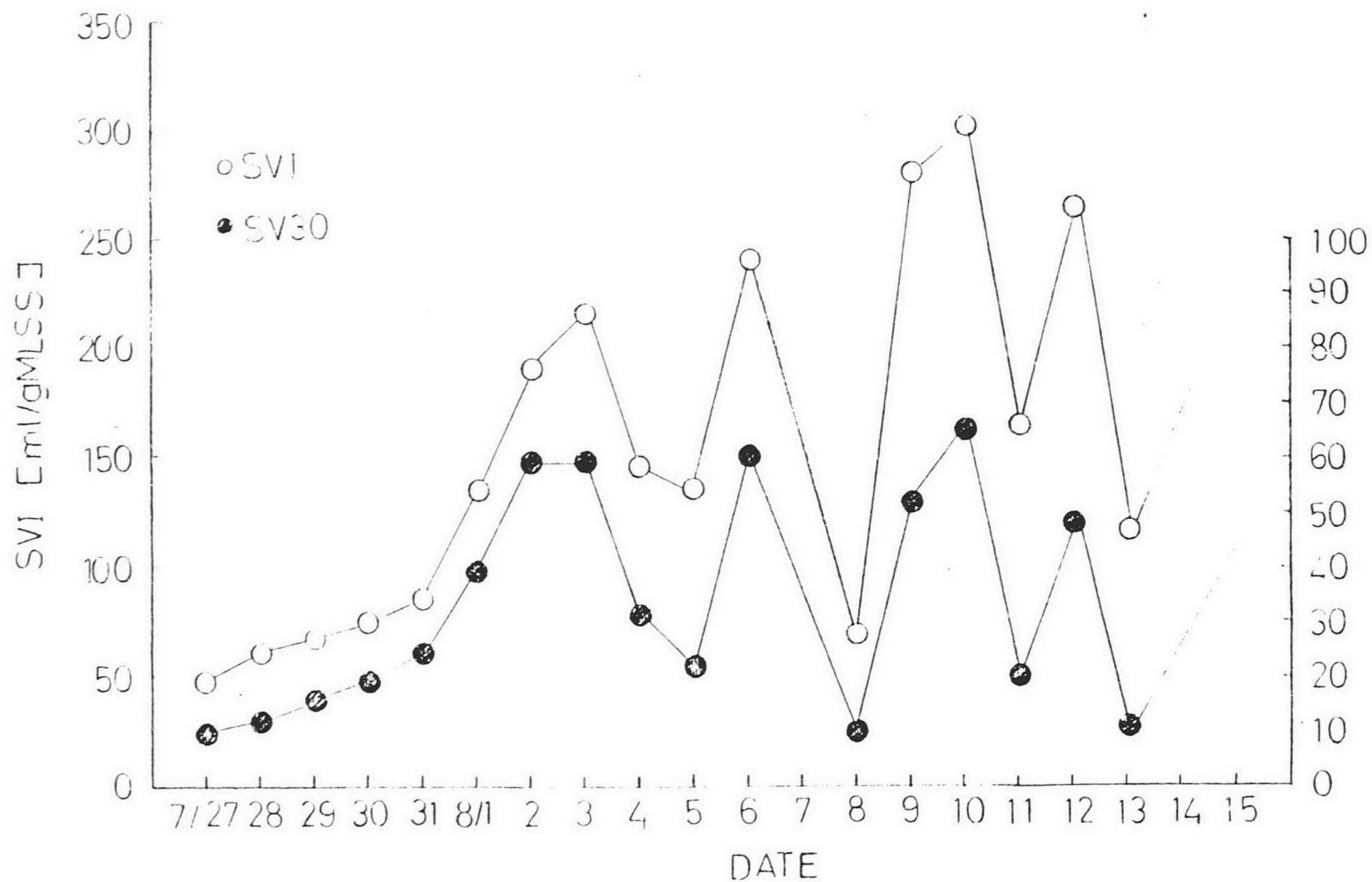
Fig 2.50   SVI & SV30   II   (7/27 ~ 8/15)
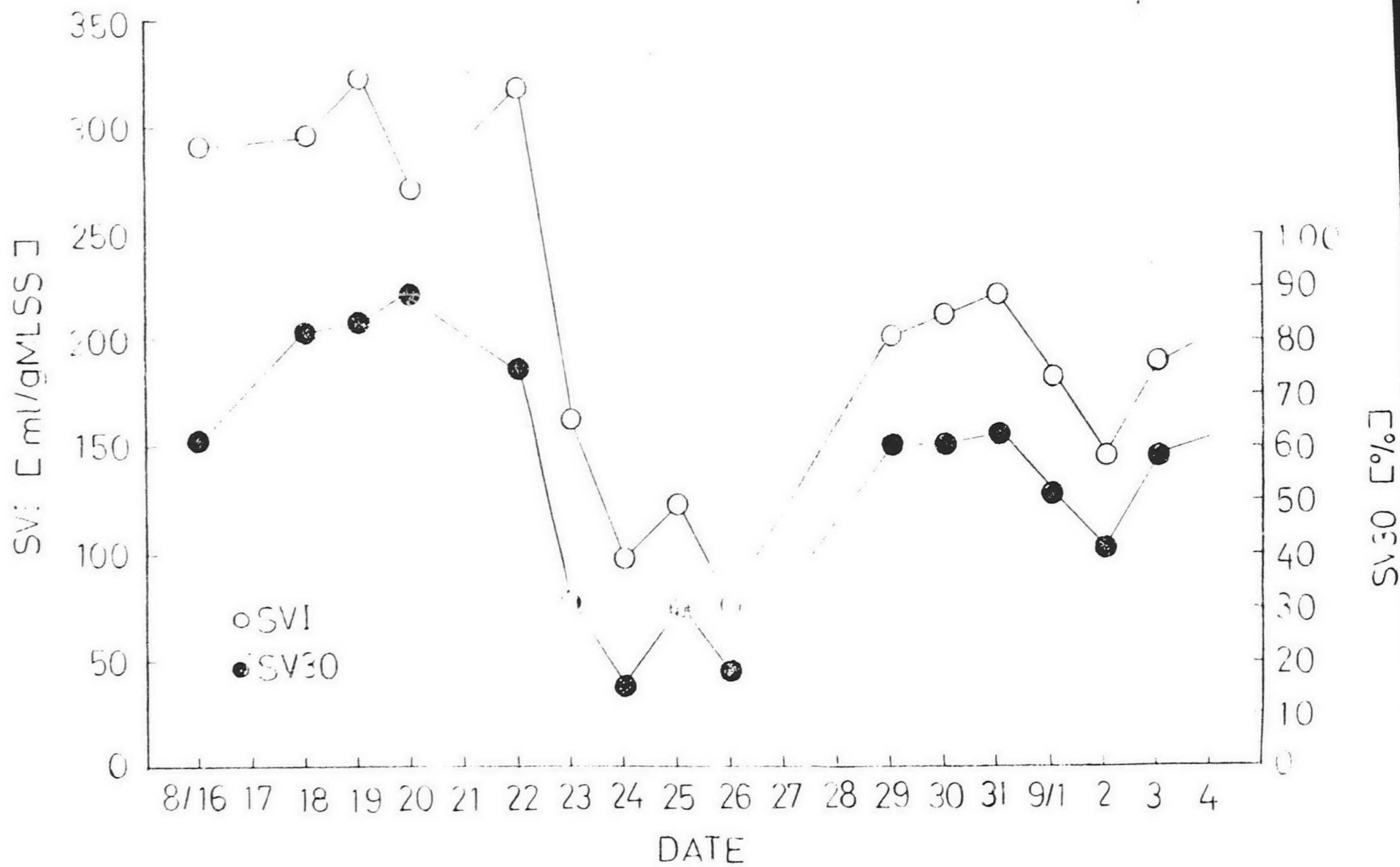
Fig. 2.51   SVI & SV30   III   (8/16 ~ 9/4)
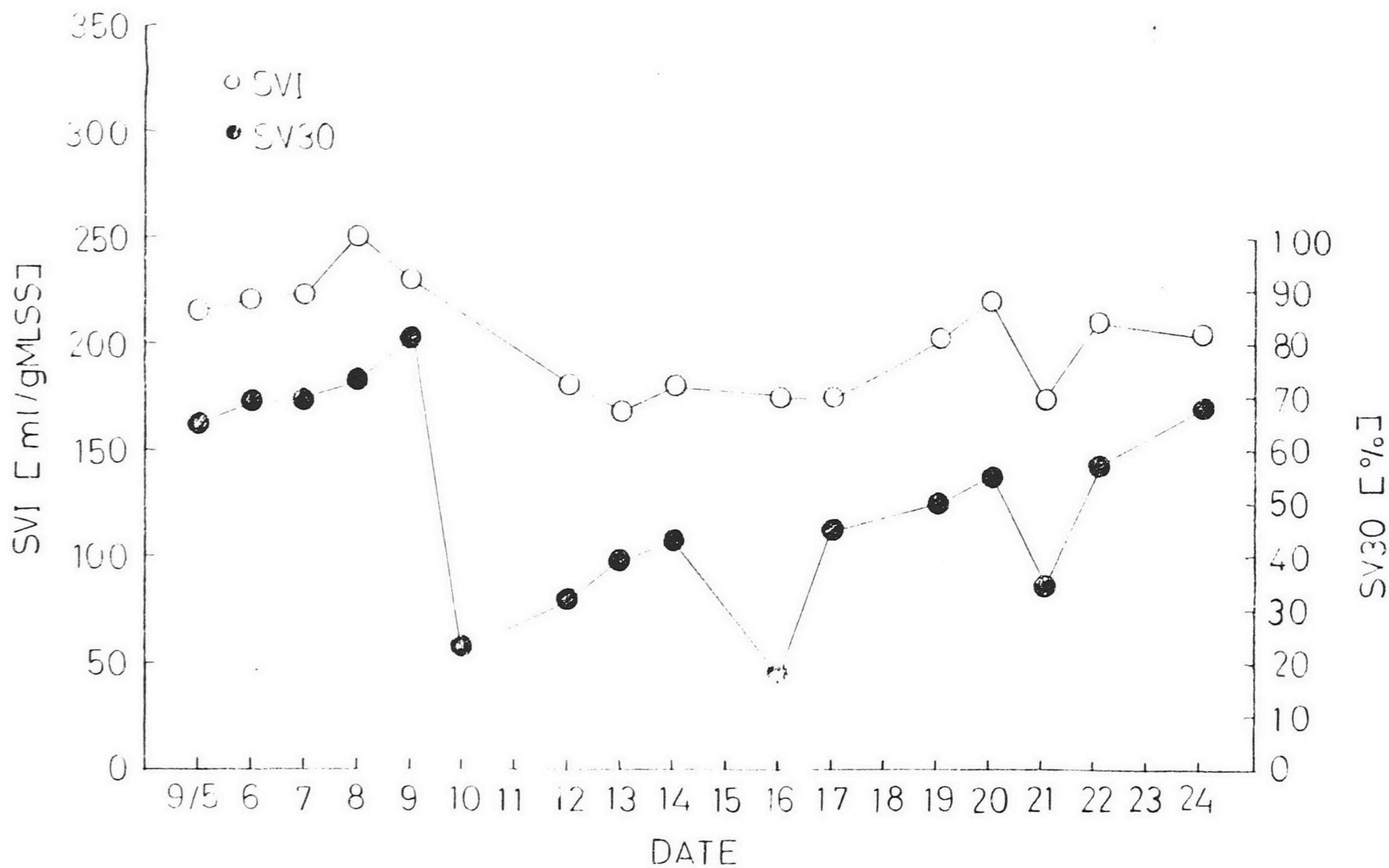
Fig. 2.52   SVI & SV30   IV   (9/5 ~ 9/24)
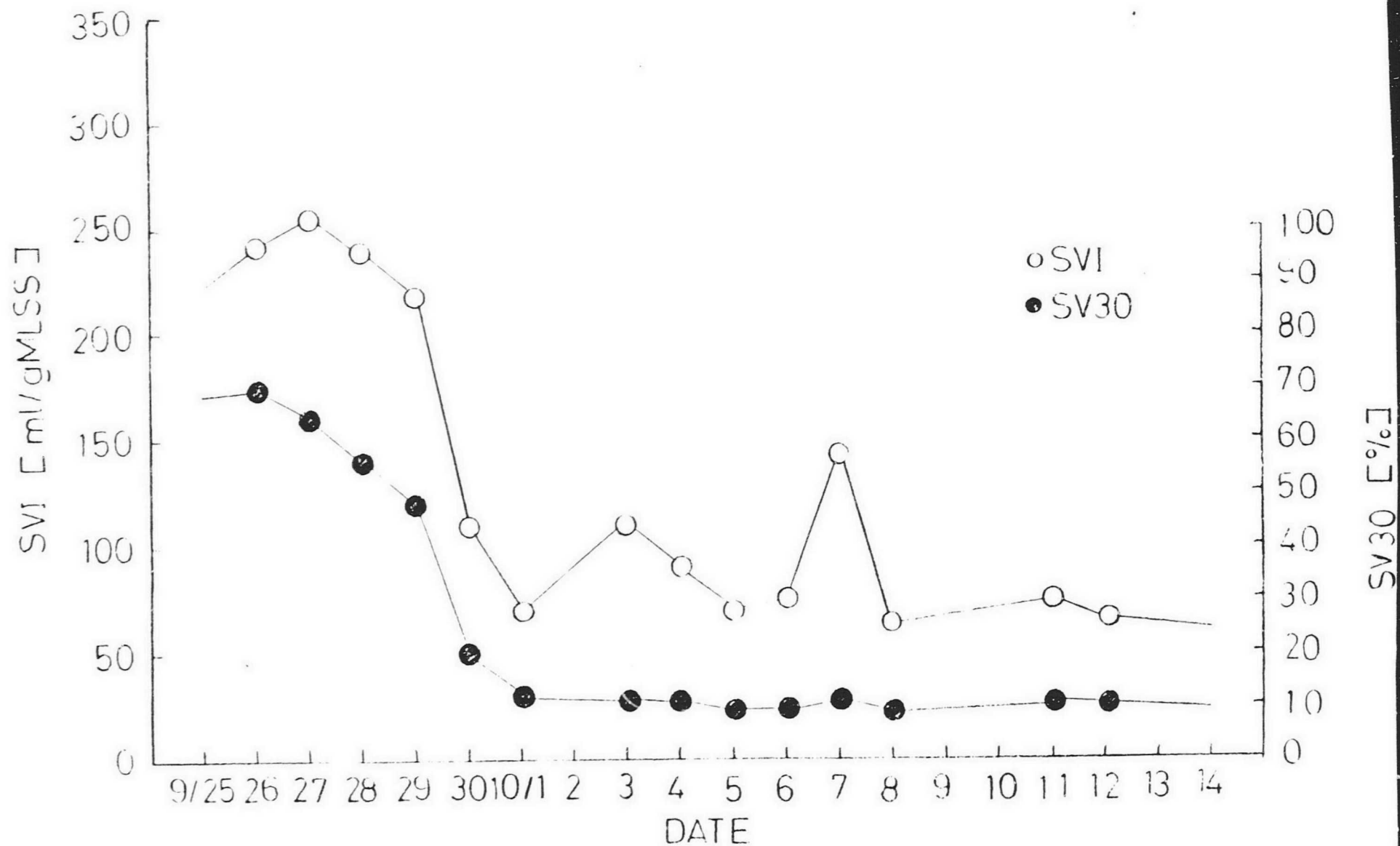
Fig 2.53   SVI & SV30 V   (9/25 ~ 10/14)
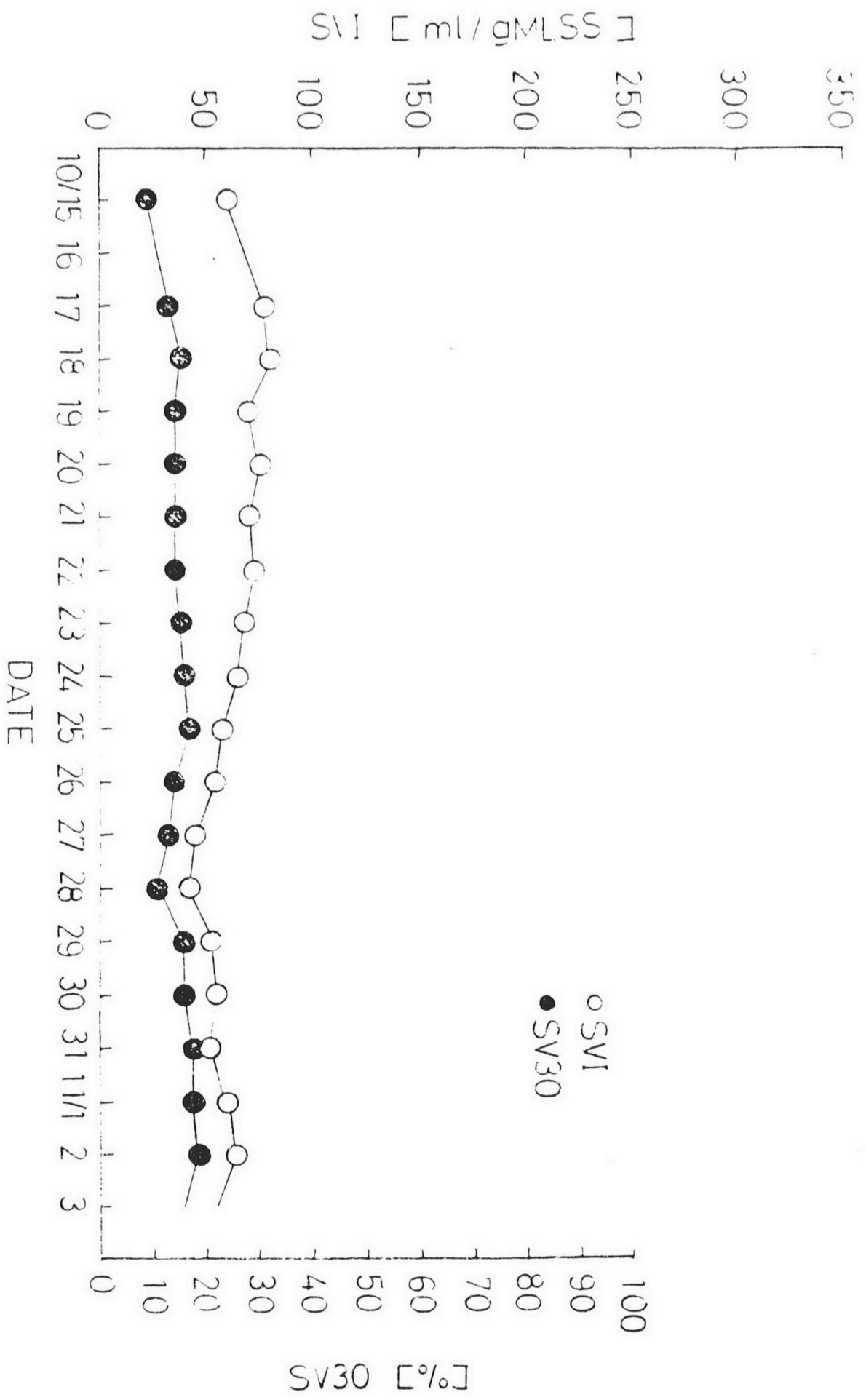
Fig. 2.54   SVI & SV30   VI   (10/15 ~ 11/3)
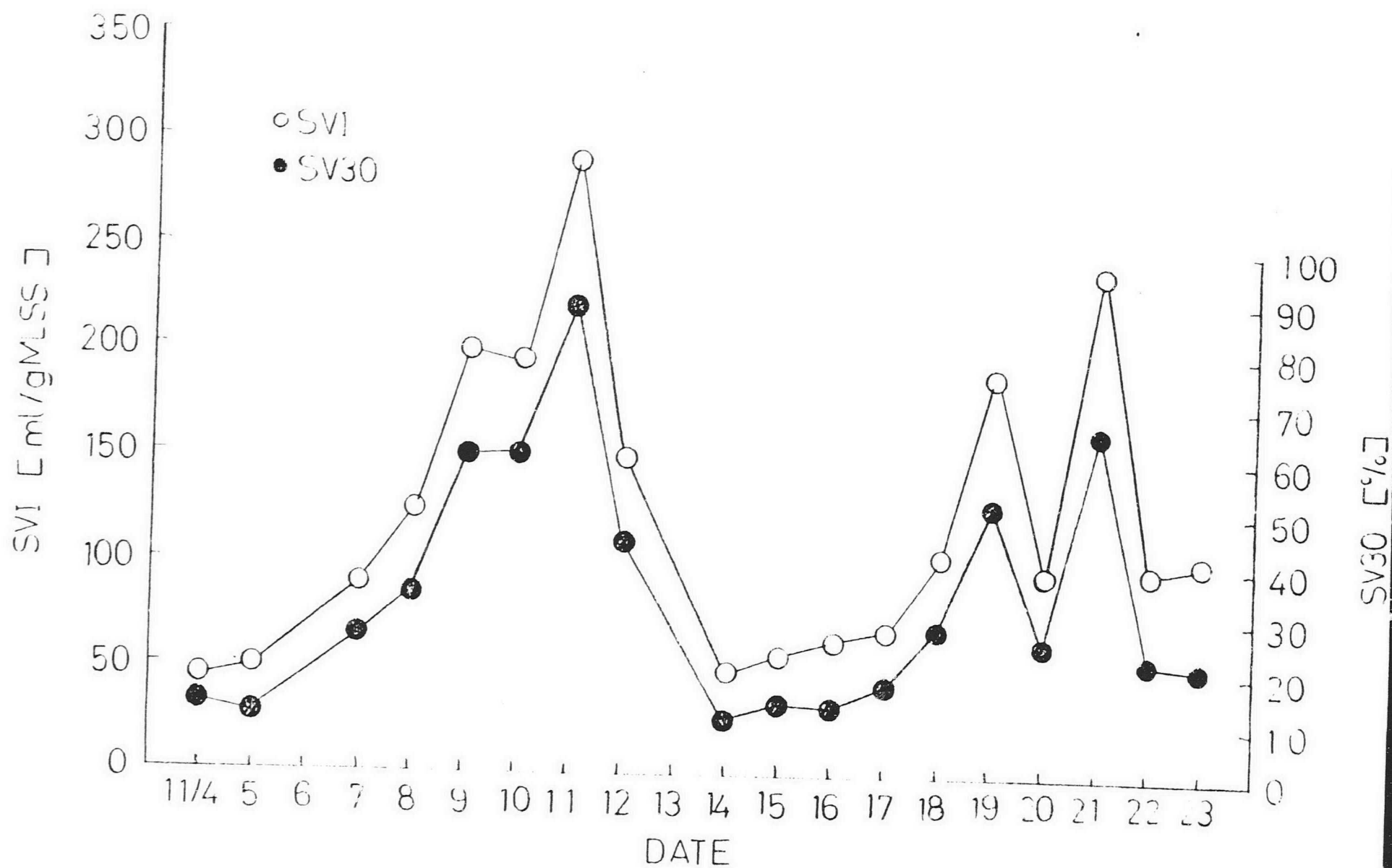
Fig. 2.55   SVI & SV30 VII (11/4 ～ 11/23)
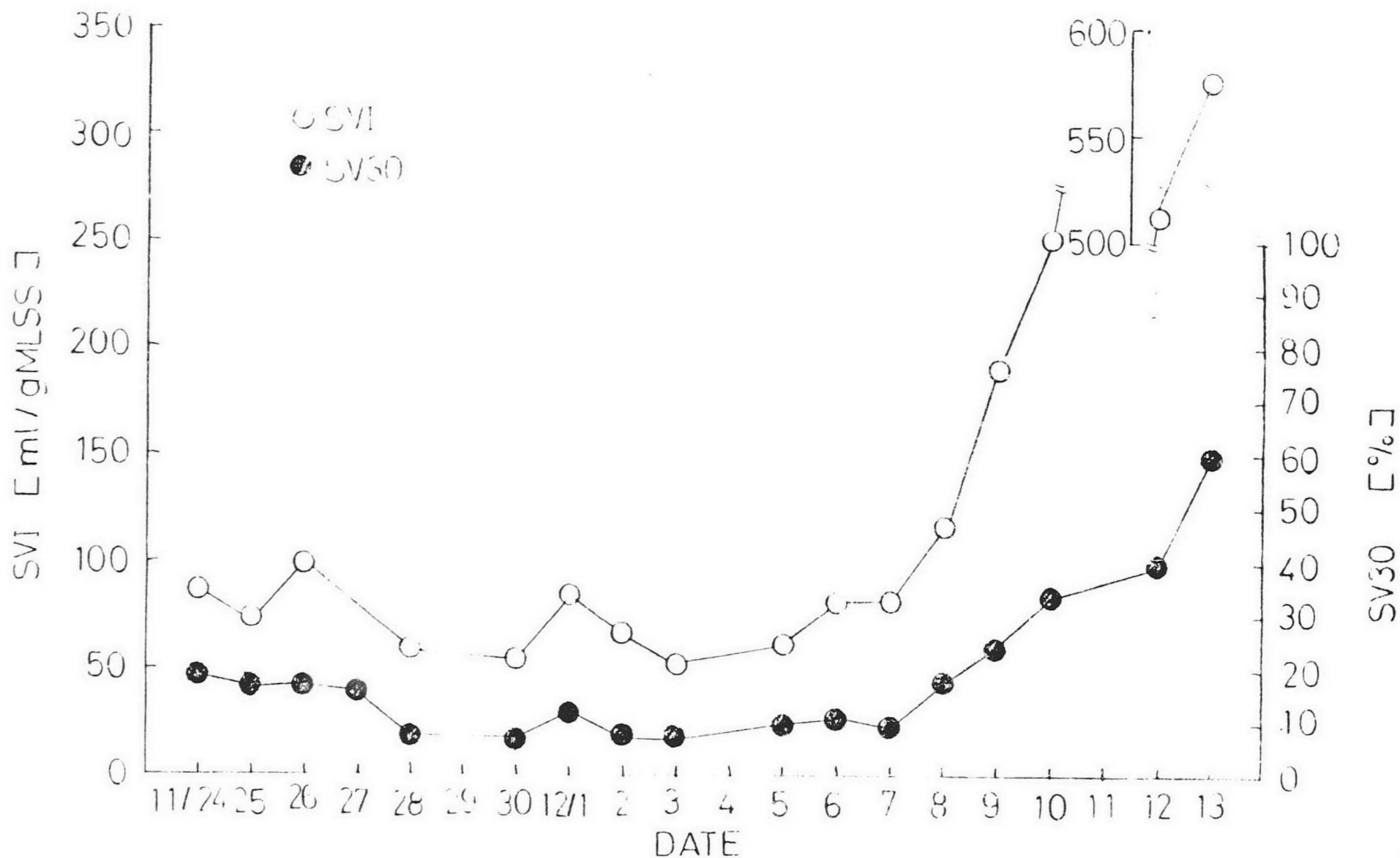
Fig. 2.56   SVI & SV30   VIII (11/24 ~ 12/13)

MLSS　　[ppm, mg/l]

Fig.2.57.　　MLSS Ⅰ　(7/7 ～ 7/26)

DATE
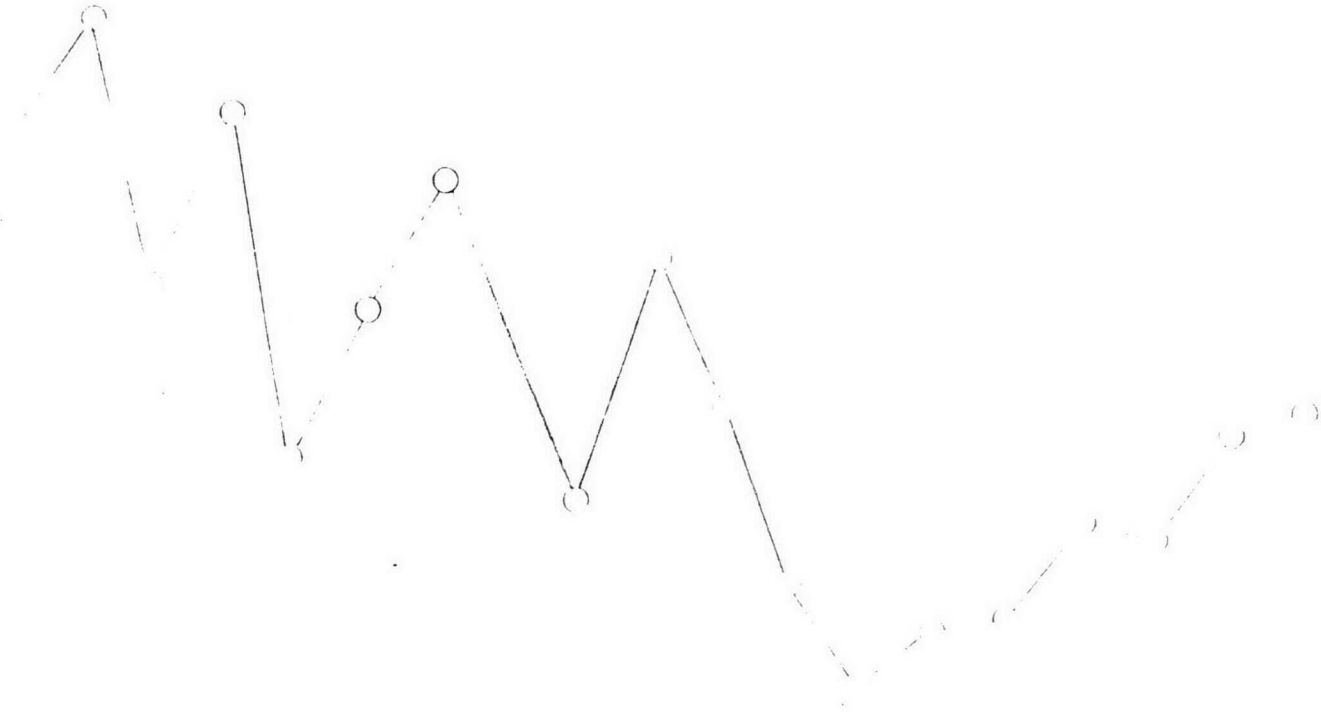
Fig. 2.58   MLSS   II   (7/27~8/15)
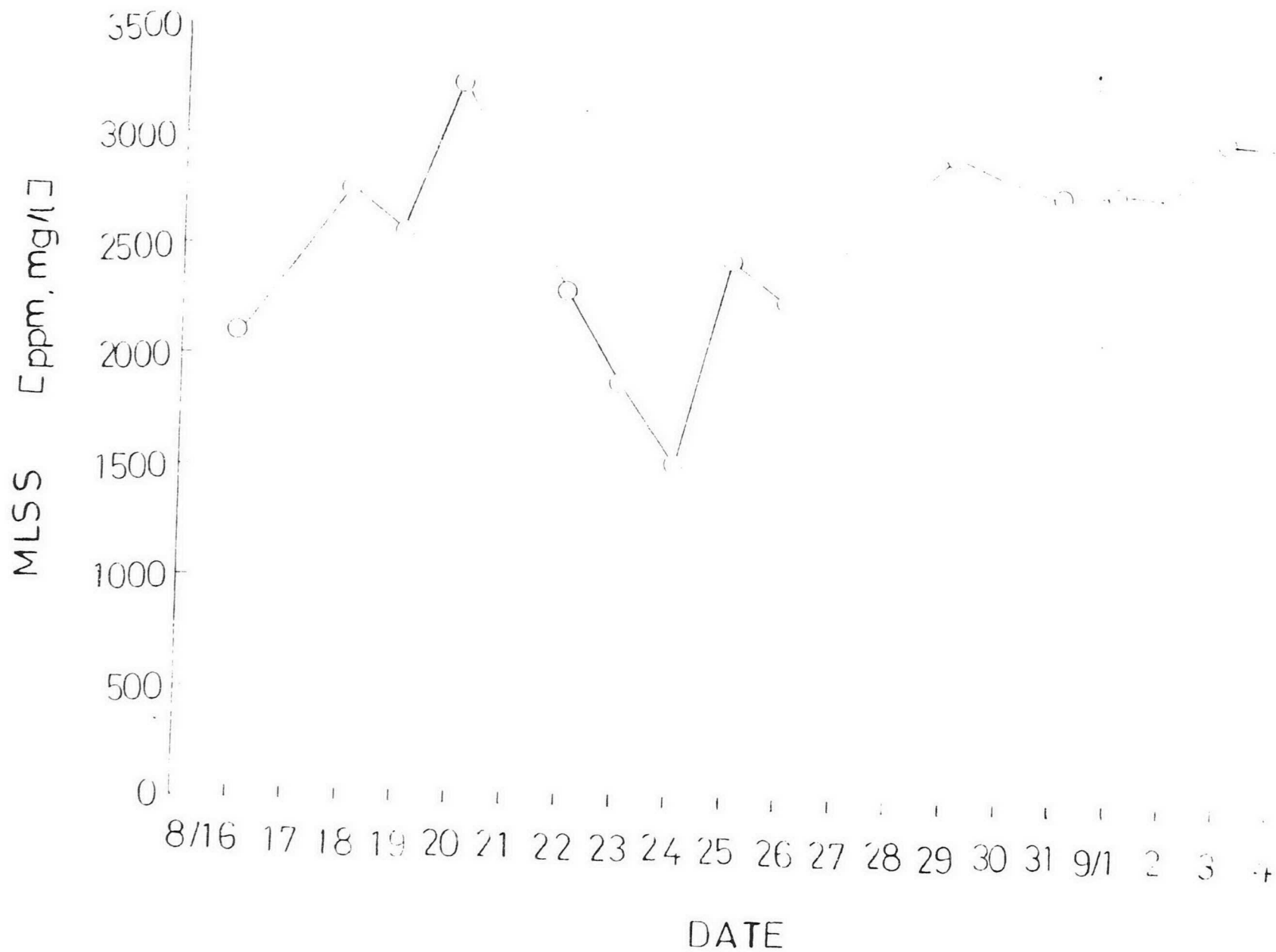
Fig. 2. 59   MLSS   III   (8/16 ~ 9/4)

Fig.2.60   MLSS   IV   (9/5~9/24)
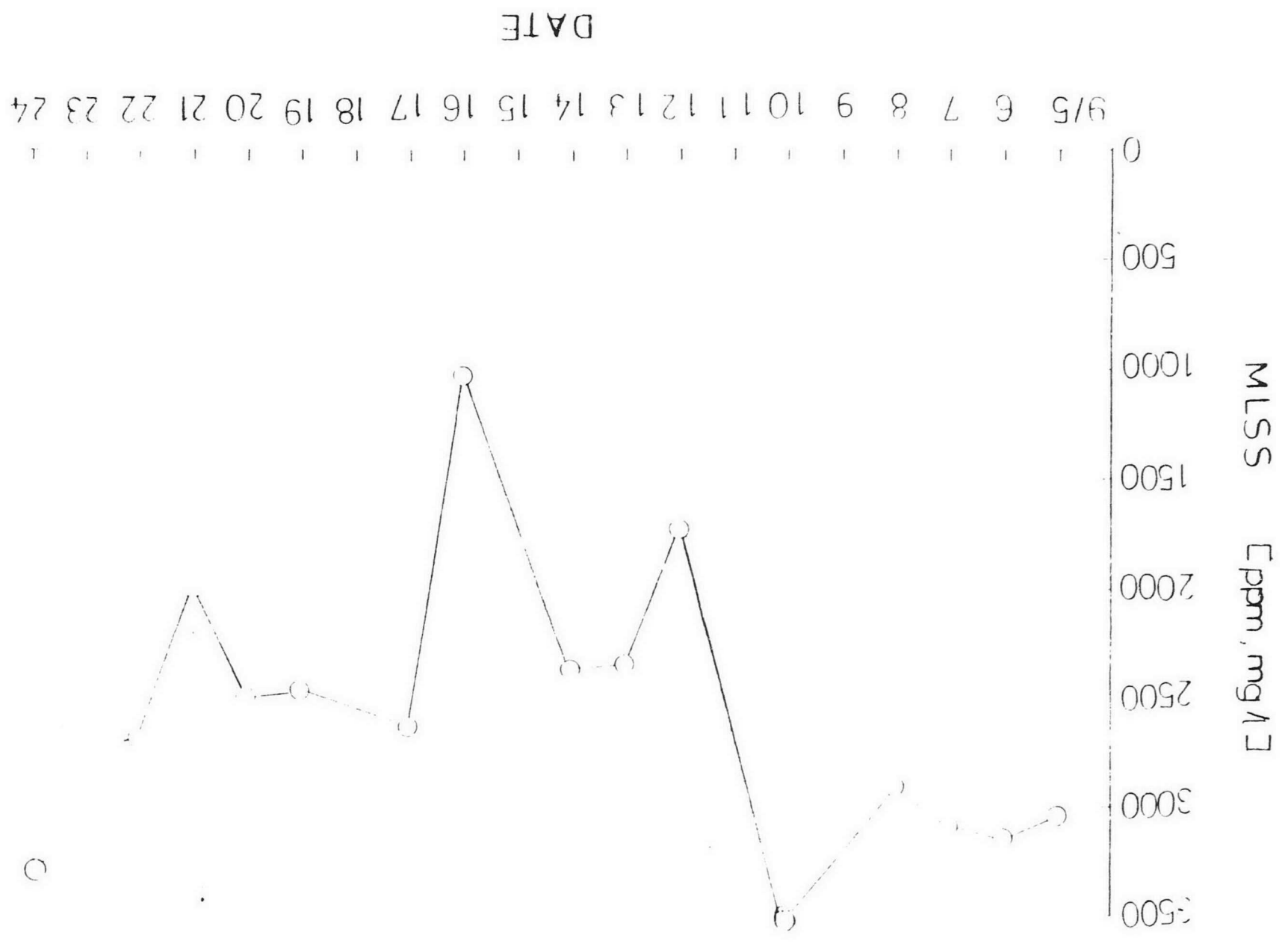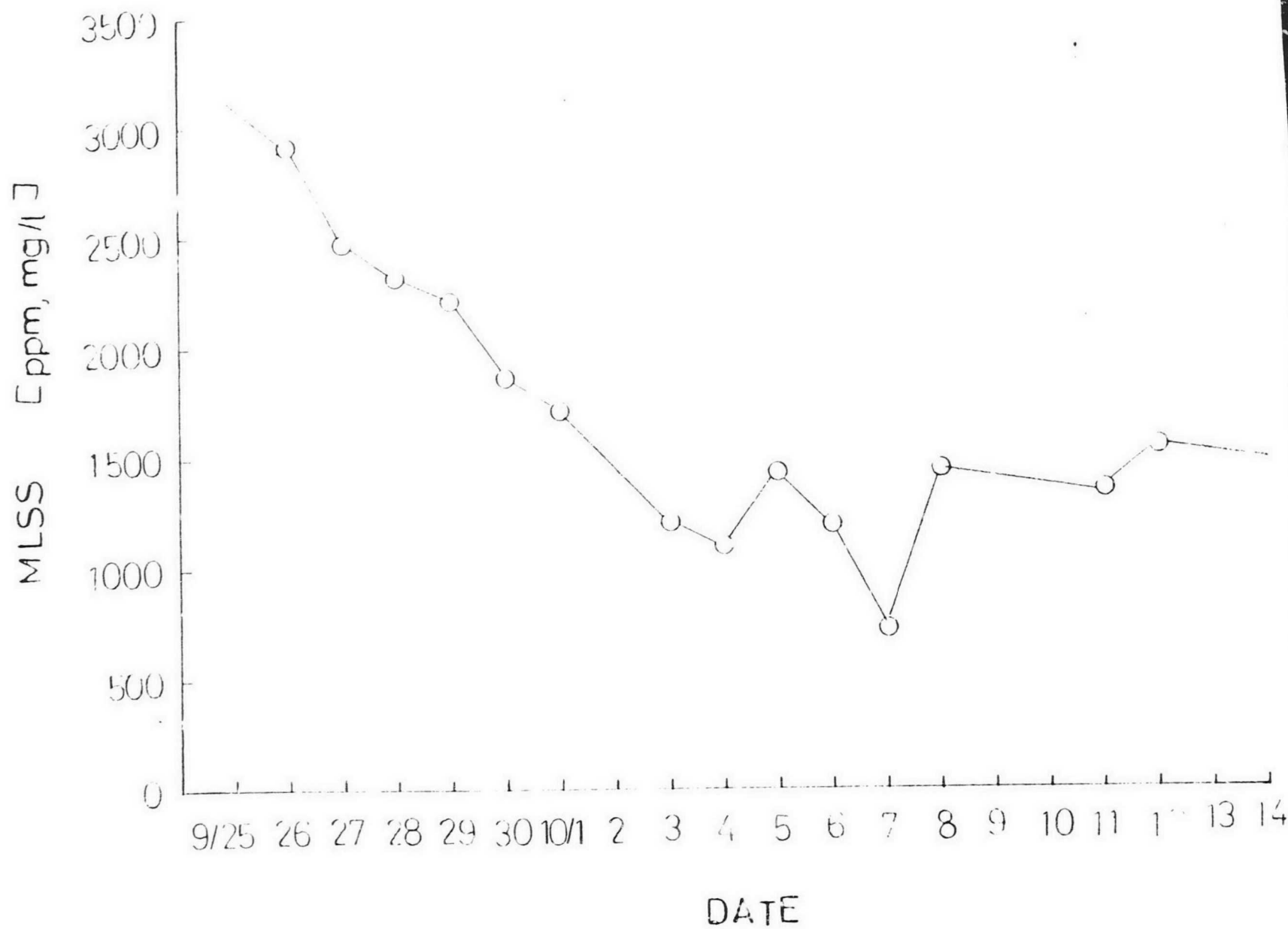
Fig. 2.61   MLSS   V   (9/25 ~ 10/14)
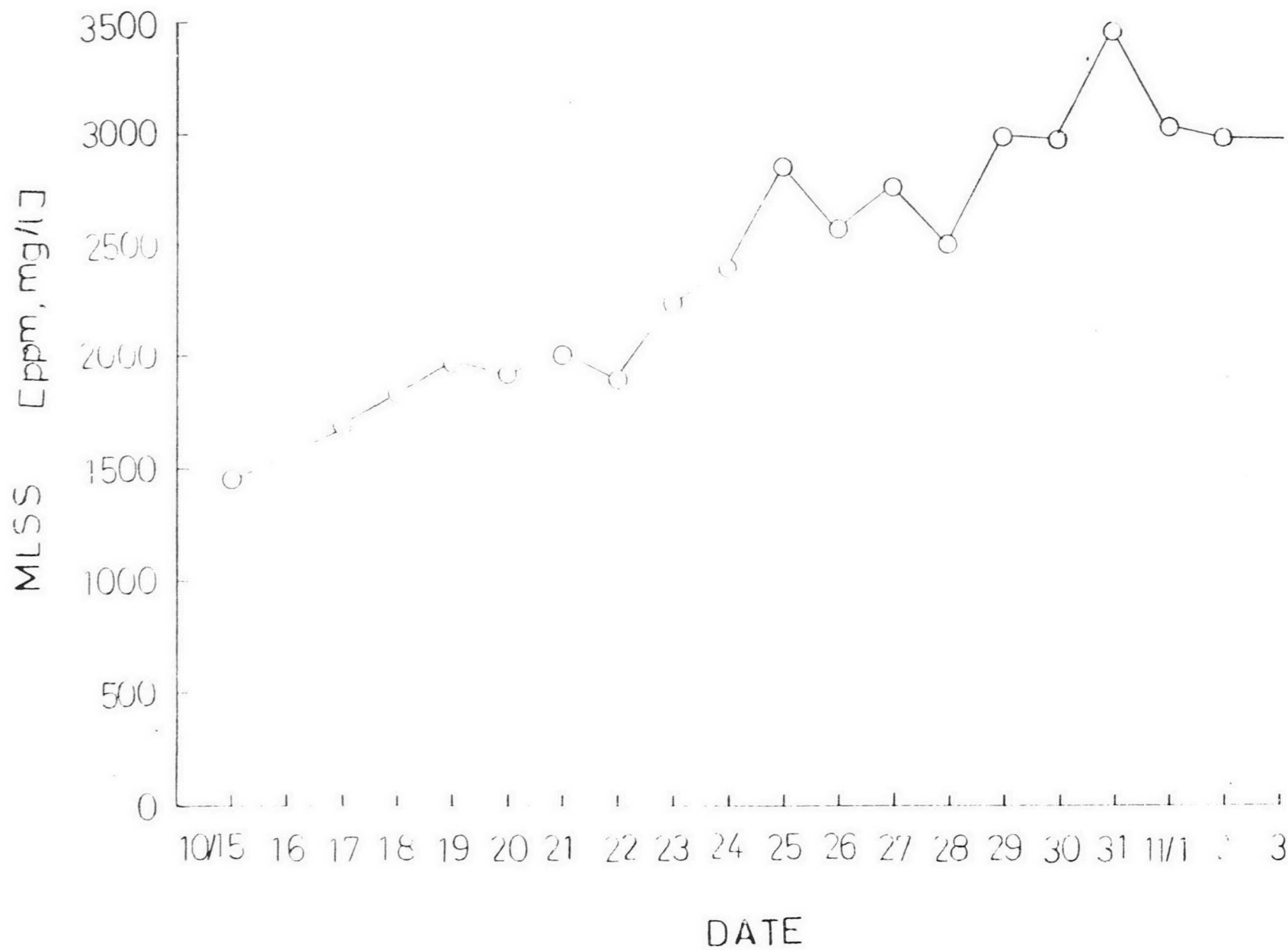
Fig. 2.62   MLSS   VI   (10/15~11/3)
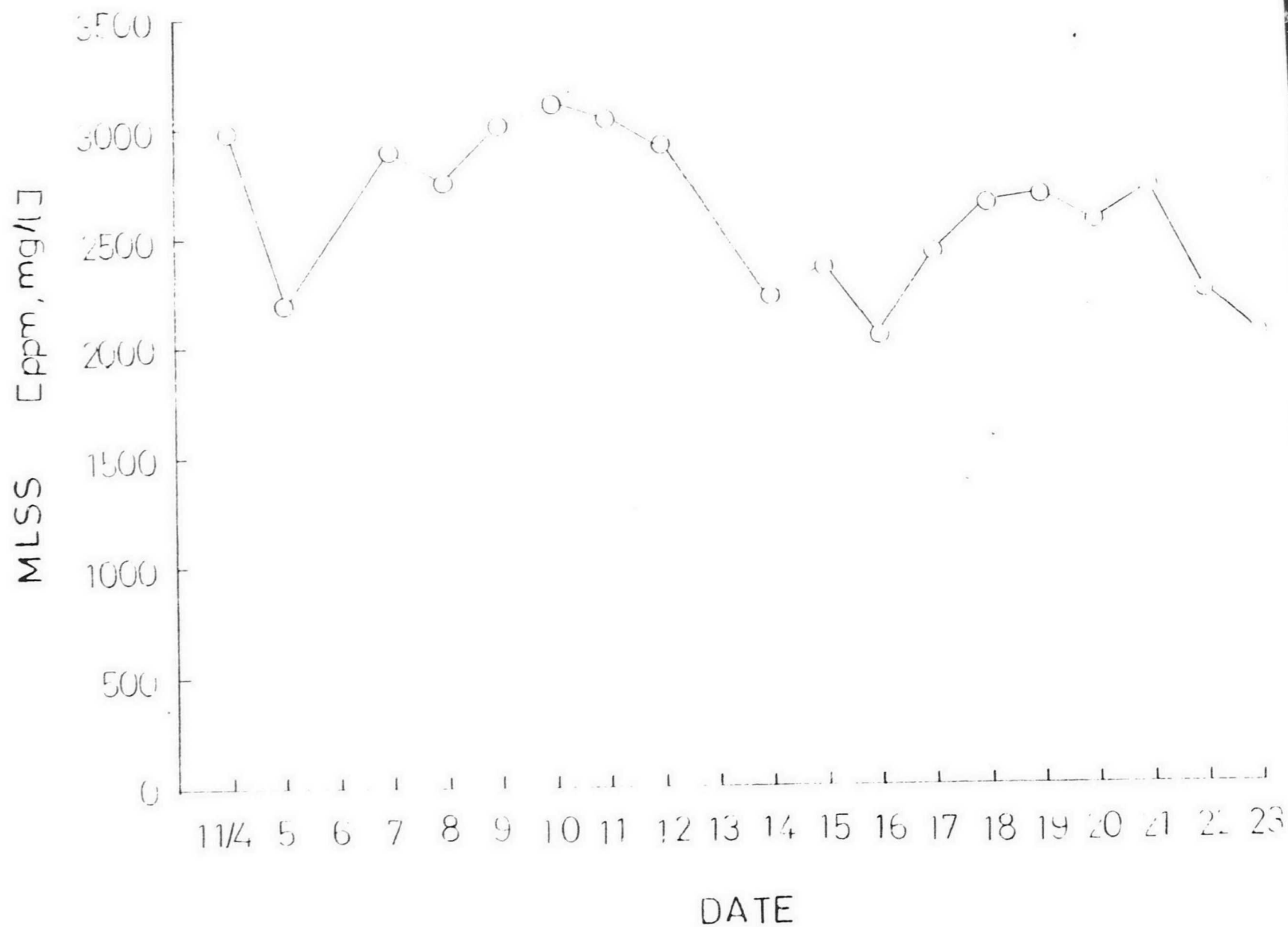
Fig. 2.63   MLSS VII   (11/4 ~ 11/24)
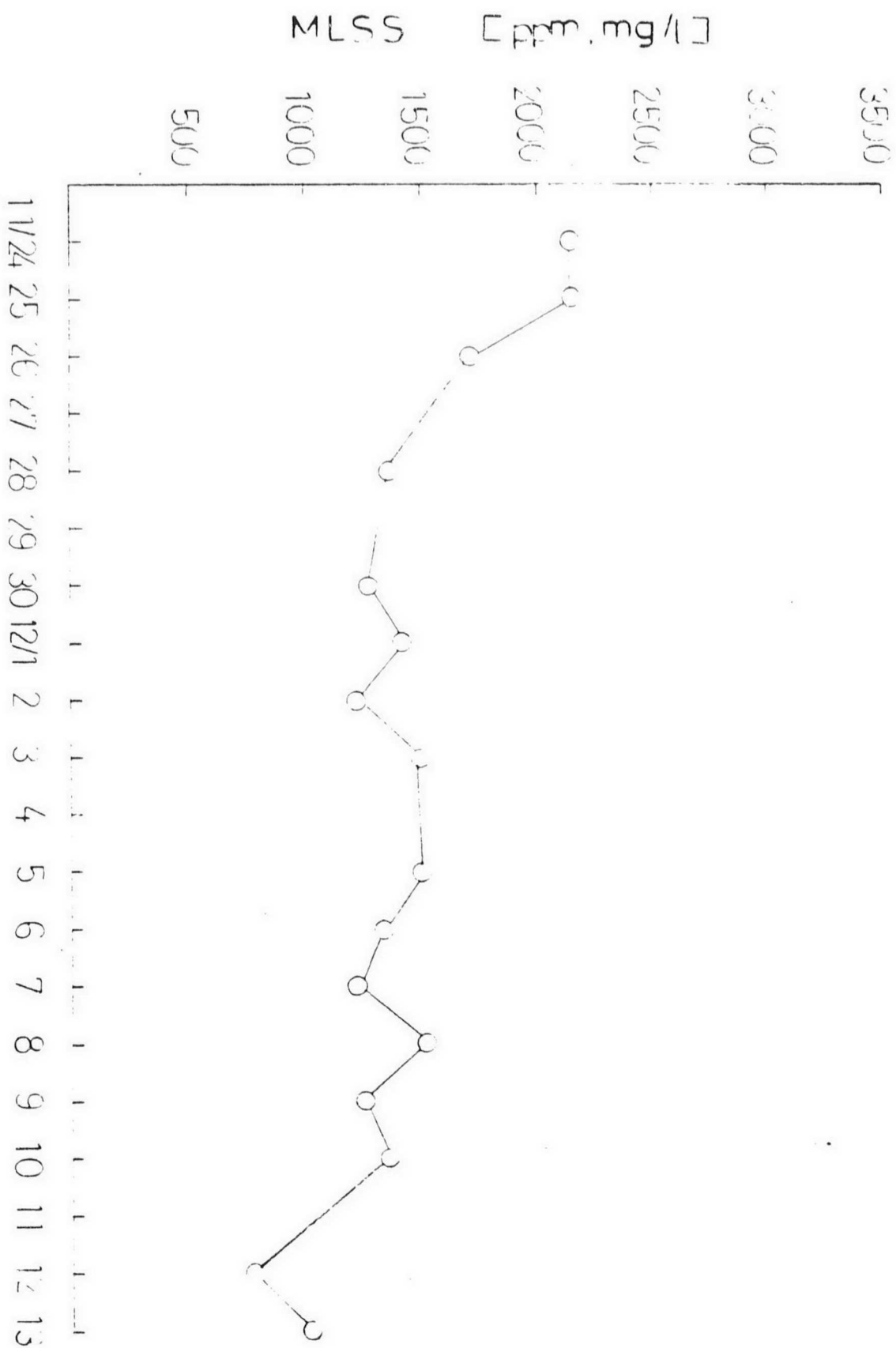
Fig.2.64 MLSS VIII (11/24 ~ 12/13)
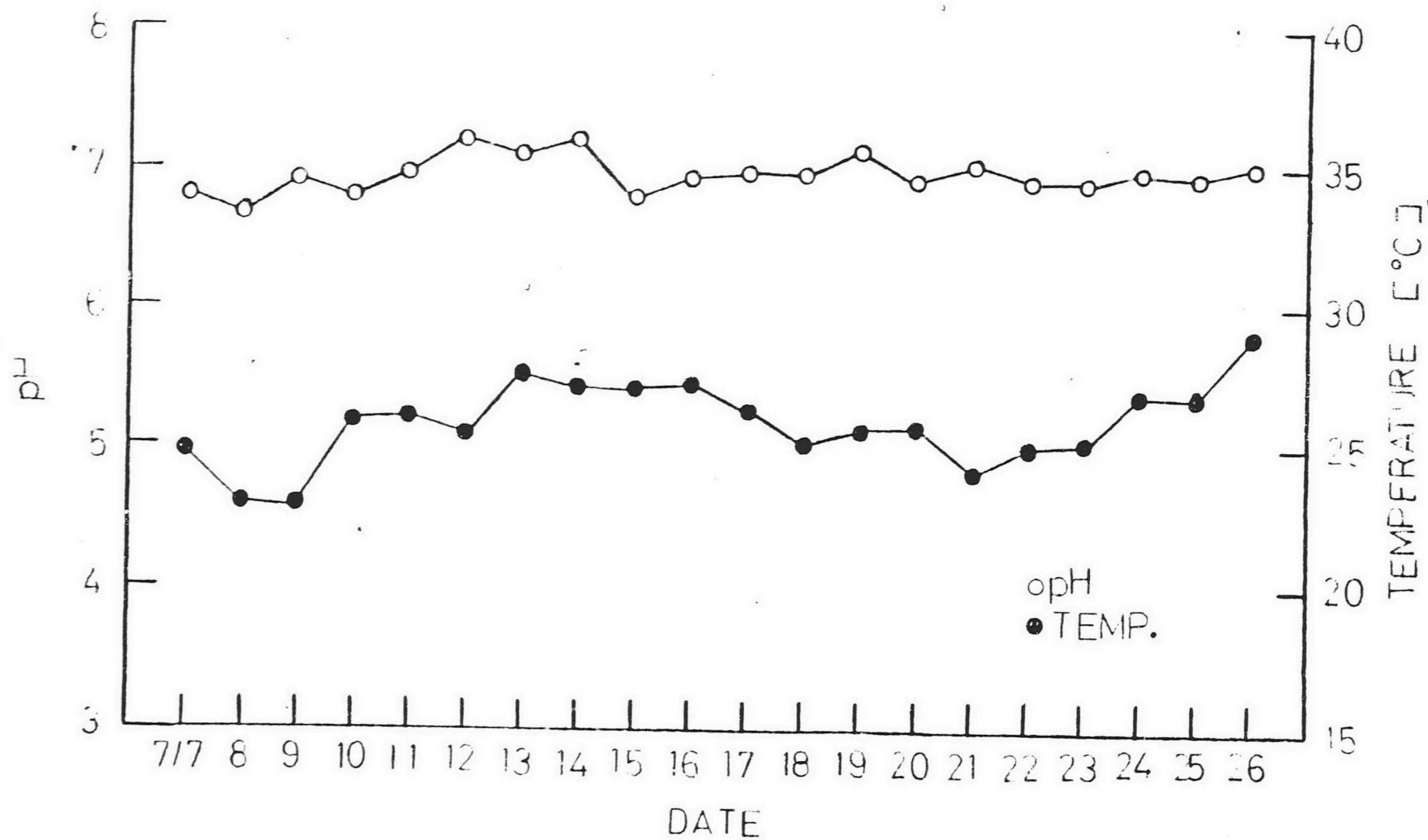
Fig. 2. 65   pH & TEMPERATURE I   ('7/7 ~ 7/26)
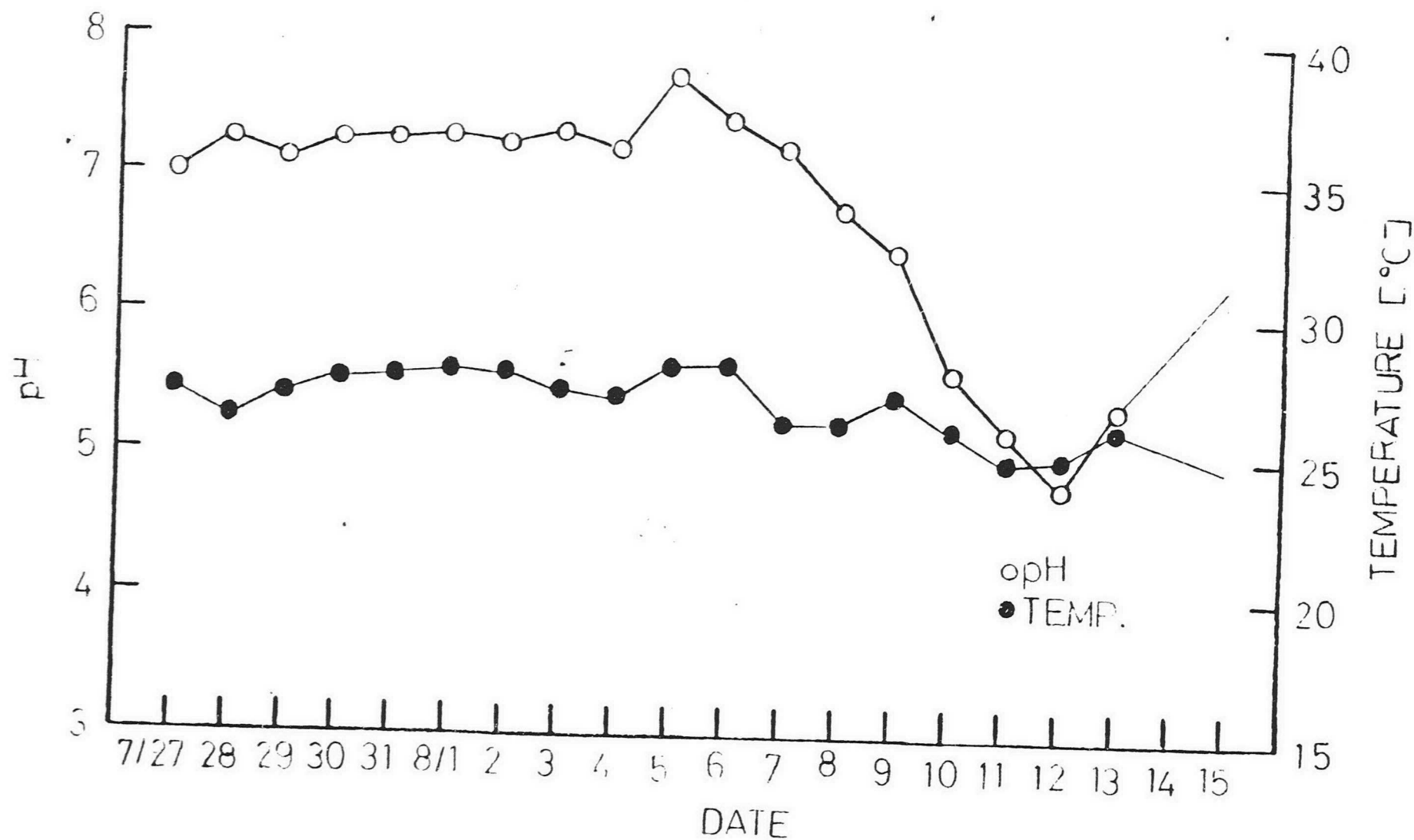
Fig. 2.66   pH & TEMPERATURE II (7/27 ~ 8/15)
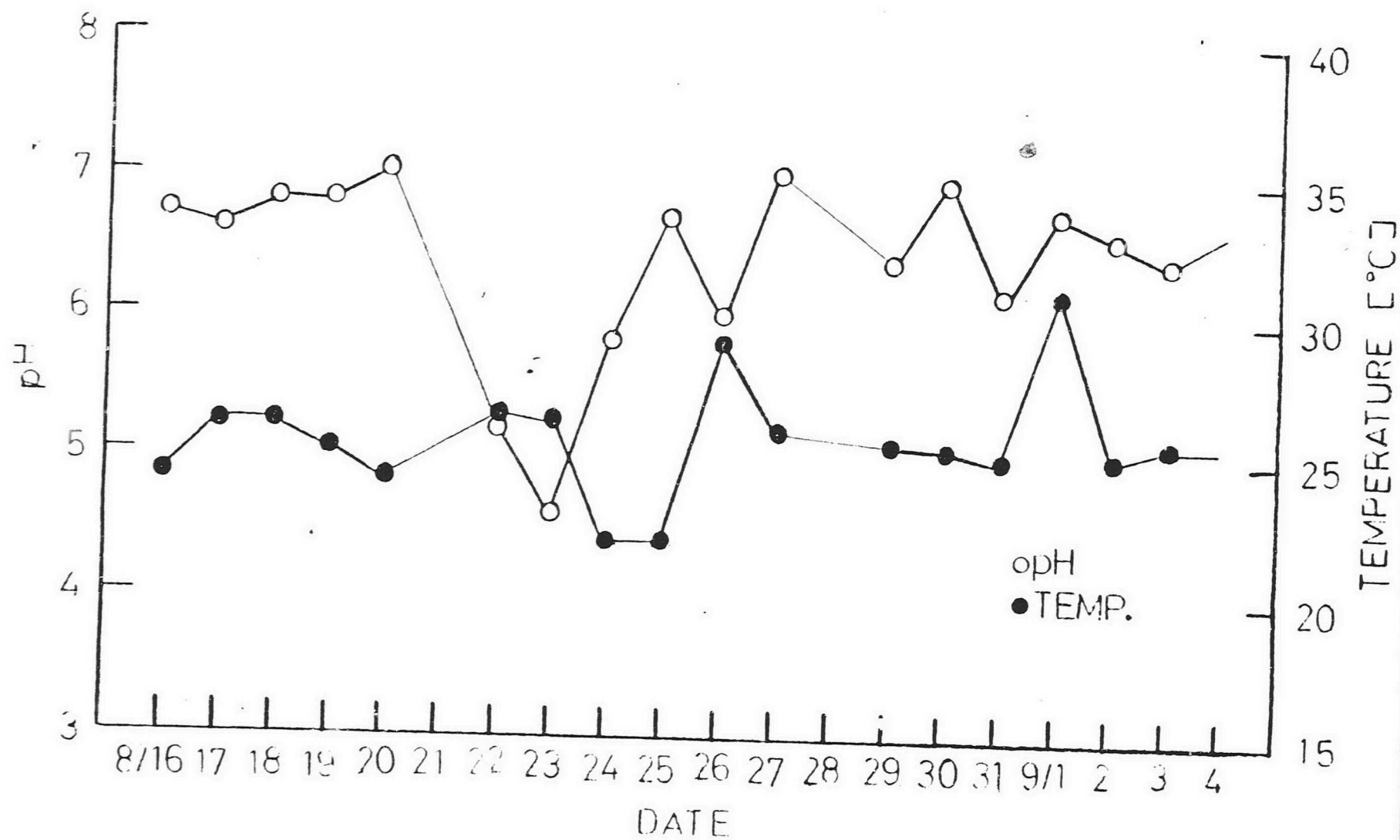
Fig. 2.67   pH & TEMPERATURE III (8/16 ~ 9/4)
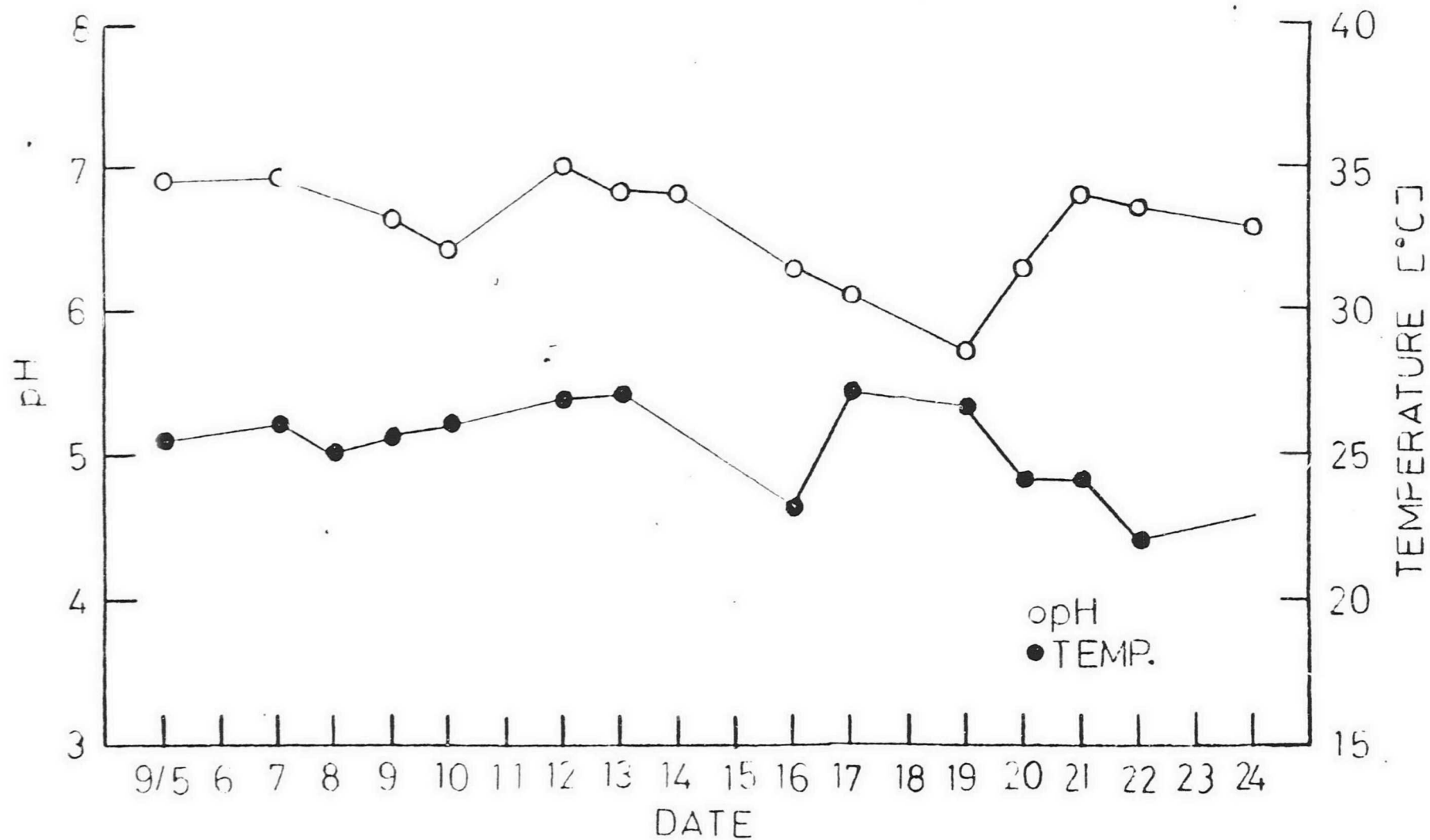
Fig. 2.68   pH & TEMPERATURE LV (9/5~9/24)
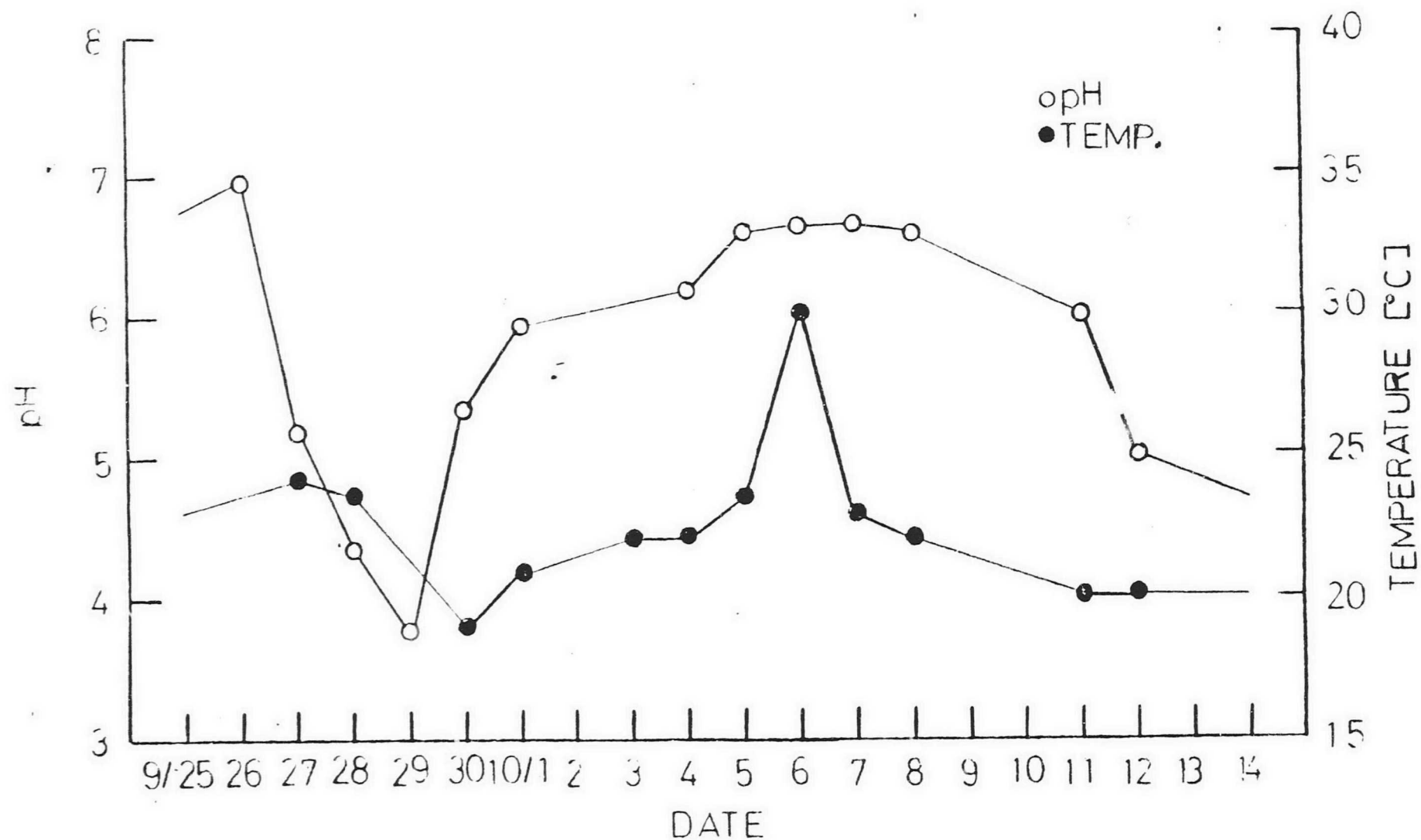
Fig. 2. 69   pH & TEMPERATURE V (9/25 ~ 10/14)

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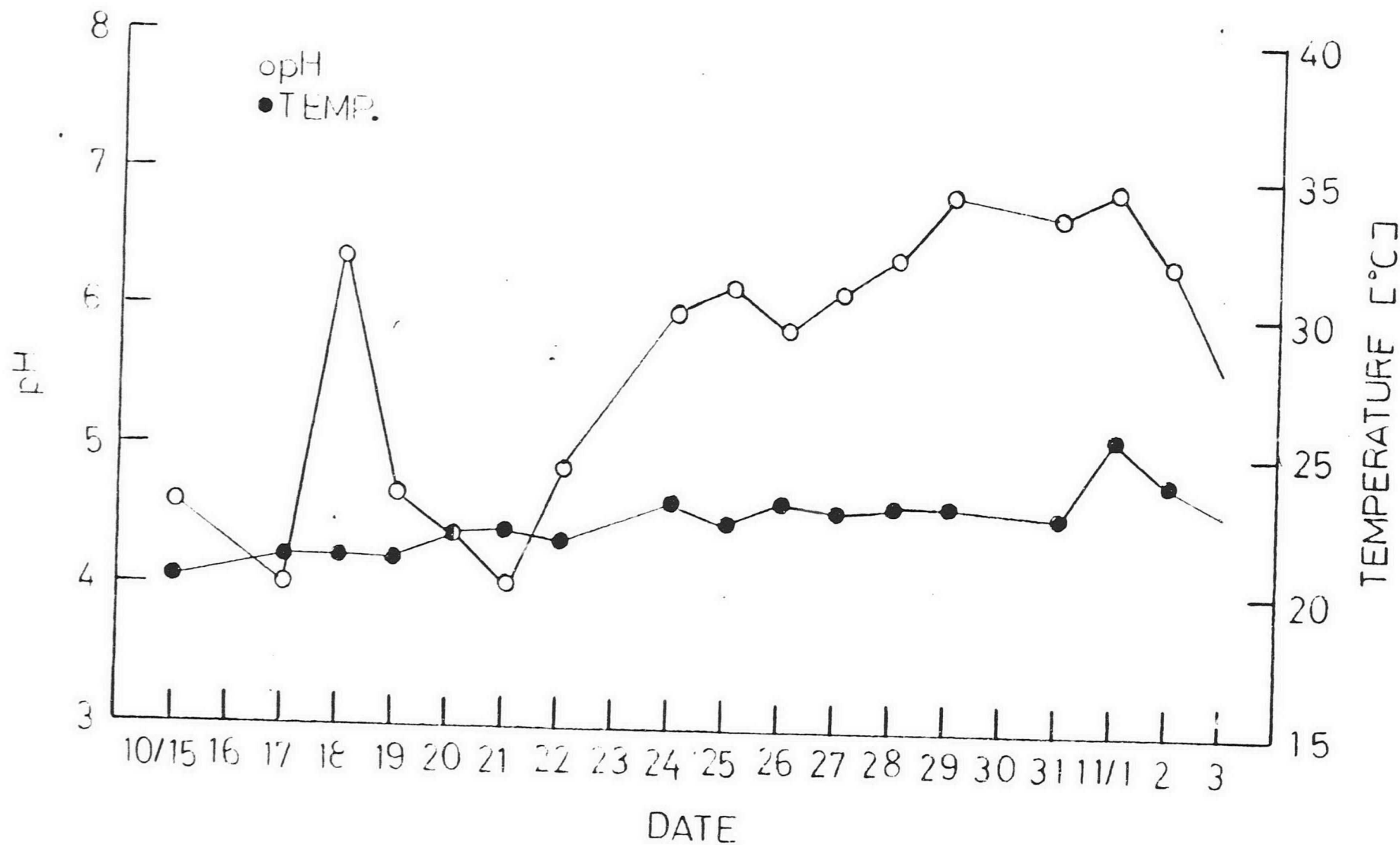
Fig. 2.70   pH & TEMPERATURE V1 (10/15 ~ 11/3)
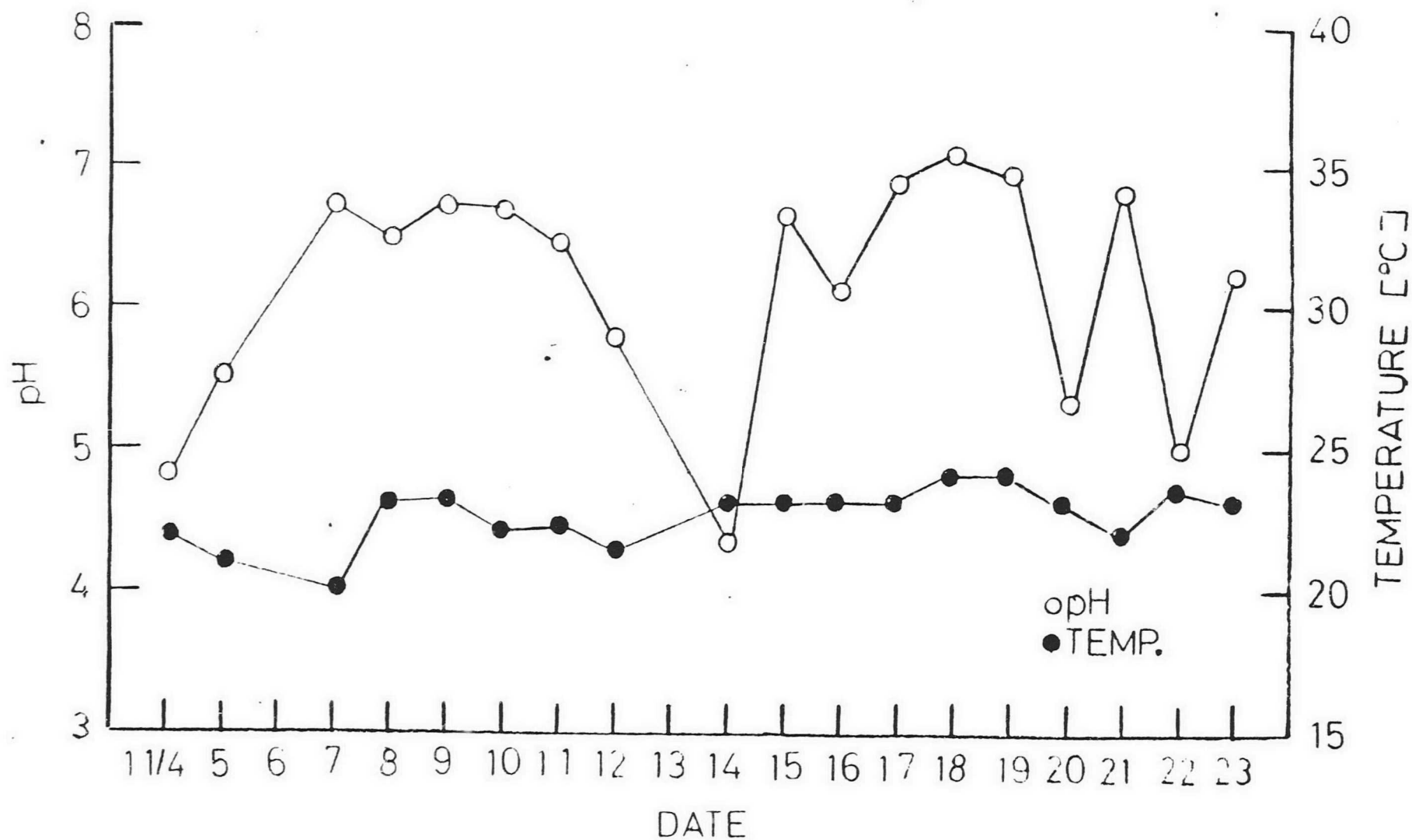
Fig. 2.71   pH & TEMPERATURE   VII   (11/4 ~ 11/23)
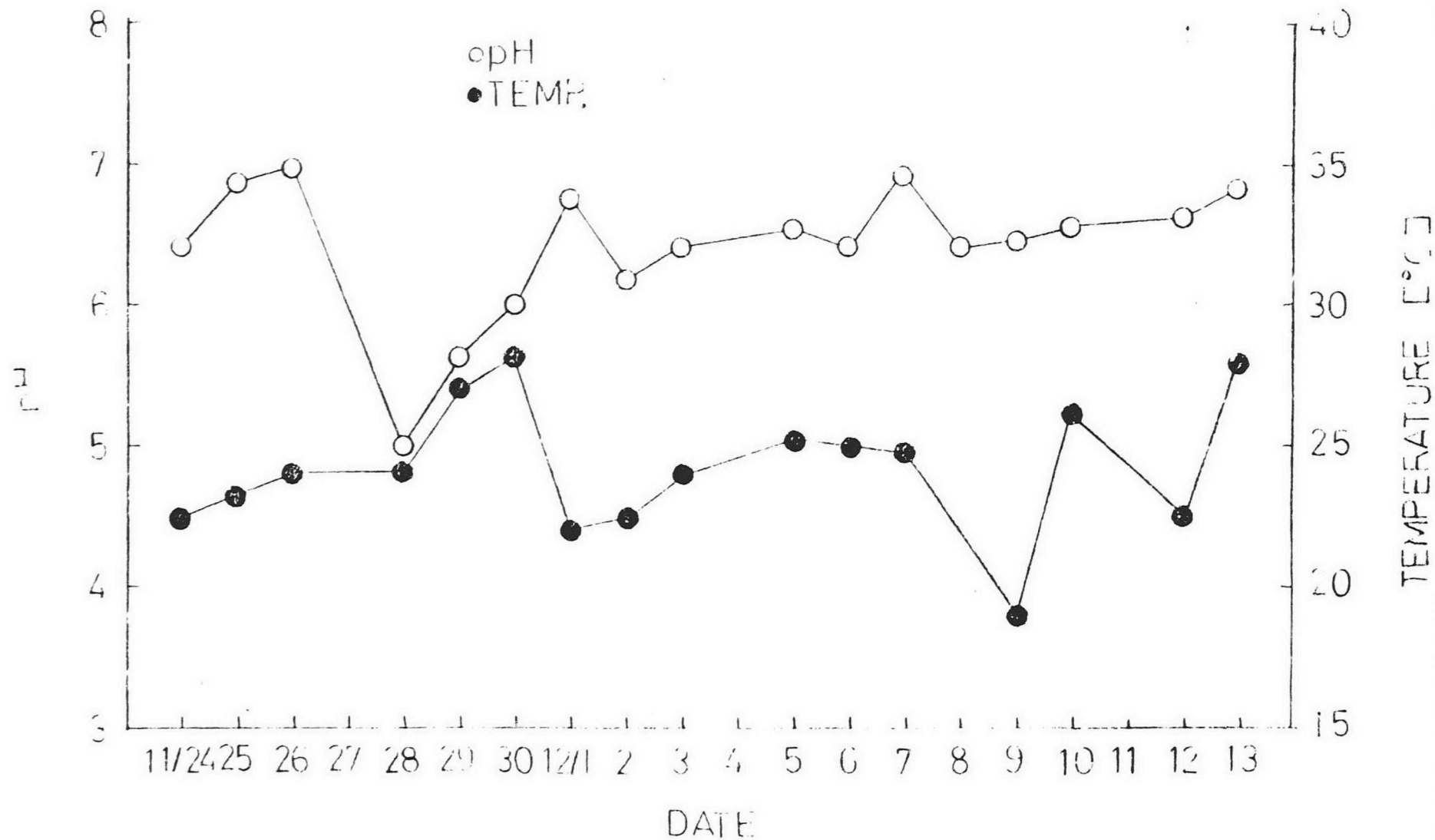
Fig. 2.72   pH & TEMPERATURE   VIII (11/24 ~ 12/13)

3. Chemical and Biological Oxidations of Aniline, Tolylene
   diisocyanate, Triethylene diamine, Glucose, and Corn-
   steep-liquor

3.1 Introduction

Biological Oxygen Demand (BOD) is not only an index of
water pollution but also a measure of biological degradation
of matters under aerobic conditions. Its detail meaning
and kinetics have been described in a preceding chapter.
In this chapter the biological oxidation of tolylene
diisocyanate (TDI), triethylene diamine (TED), glucose,
and corn steep liquor (CSL) is given   as a function of
BOD.

If the efficiency of biological oxidation is high, the
matter would be a substrate for the biological treatment.
Chemical Oxygen Demand (COD) is an index of chemical
oxidizability of matter. COD of hydrolyzed TDI, TED,
aniline, glucose, and CSL was also measured.
The corelations among BOD, COD, and TOD (Total Oxygen
Demand which is obtained from calculation)were discussed.
Aniline, glucose, and CSL were examined for the purpose
of comparison with TDI and TED.

3.2 Experimental

The measurement of BOD was conducted according to JIS (Japanese Industrial Standard). The following four solutions were prepared.

Buffer solution (A)

K_2HPO_4 (21.75 g), KH_2PO_4 (8.5 g), $Na_2HPO_4 \cdot 12H_2O$ (44.6 g), and NH_4Cl (1.7 g) were dissolved into water and the solution was so diluted that its volume attained 1L. pH of the solution was 7.2.

Solution of magnesium sulphate (B)

The solution containing 22.5 g $MgSO_4 \cdot 7H_2O$/L was prepared.

Solution of calcium chloride (C)

The solution containing 27.5 g/L was prepared.

Solution of ferric chloride (D)

The solution containing 0.25 g $FeCl_3 \cdot 6H_2O$/L was prepared.

Procedure

Sample should be prepared immediately before BOD measurement.

If the sampling solution is too concentrated for BOD measurement, it is diluted approximately by de-ionized water until its total volume was brought to 300 ml. Then, the seed solution, A, B, C and D were added.   Seeds used in this experiment usually were a supernatant of activated sludge solution, and added 3 ml. Activated sludge mixture solution

was also used for a few runs.

. . Usually activated sludge was cultured with continuous feeding.
The difference in activated sludge conditions may not
change BOD values seriously.

Secondly, 3 ml of the buffer solution of A was added for
maintaining pH within 7.2 - 7.4. One ml of B, C, and D
solutions were added as nutrients for microorganisms.
At the same time, standard reference solution for BOD
measurement should be prepared.

Three hundred ml. of glucose solution was diluted with
de-ionized water to 3×10^{-4} wt.% and A,B,C a D solutions
were added respectively, as the same volume of the samp..
solutions.

Five samples with different silutions and a
standard reference solution may be incubated at the same
time.

The incubating room was maintained at $20^{o}C$. The incubator
was always stirred by magnet stirrer intensively.

Coulo-Meter generates oxygen by electrolysis of saturated
copper sulfate solution in response to the biological
oxidation of a sample. The exhausted CO_2 from incubated
sample was absorbed with soda lime so that the content of
air in the incubator may be held constant.

After the incubation, the quantity of the charge used for

electrolysis was converted into the amount of oxygen

. consumed by biological oxidation.

This value was recorded continuously.

Usually BCD measurement was continued for 5 days and its

value is referred as BOD_5.

· COD was obtained according to Japanese Standard (JIS)as follows:

Principle

To evaluate the organic materials dissolved in a solution,

$KMnO_4$ solution is added to samples and oxidizes them for a

period. Then the amount of $KMnO_4$ consumed to the oxidation

is measured by titration.

Reagents

The water used for the measurement should be de-ionized

and free from organic material.

Sulfuric acid diluted with twice volume of water is

prepared. Also, 1/40 N $Na_2C_2O_4$ and 1/40 N $KMnO_4$ solutions

should be prepared. Fine powder of Ag_2SO_4 is also needed.

Operations

A proper amount of sample solution is diluted to 100 ml

with water and adds 10 ml sulfuric acid solution prepared

before. After 0.3 g Ag_2SO_4 is added, the vessel stirred

vigorously for a few minutes. Then, 10 ml of 1/40 N $KMnO_4$

solution is added very correctly.

The vessel is heated in the boiling water for 30 minutes.

After that, 10 ml of 1/40 N $Na_2C_2O_4$ solution is added keeping the vessel 60 to 80°C.

Finally, the solution is subject to reverse-titration with 1/40 N $KMnO_4$. COD is calculated according to the equation.

$$COD = (b - a) \times f \times \frac{1,000}{V} \times 0.2$$

COD; chemical oxygen demand (ppm)

b; volume of $KMnO_4$ solution consumed to the reverse-titration of sample (ml)

a; volume of $KMnO_4$ solution consumed to the reversed-titration of blank (ml)

f; factor of 1/40 N $KMnO_4$ solution

V; volume of sample solution

3.3 Results and Discussions

Corn Steep Liquor (CSL) and Glucose

COD and BOD_5 of CSL and glucose for different concentrations are given in Table 3-1.

The effluent from activated sludge system (ASS) which was cultured with CSL was also subject to BOD_5 test.

Fig. 3-1 shows the corelation between COD and BOD_5 for CSL. As shown in this figure, BOD_5 was proportional to COD with a slope of 2.1. In other words, CSL was oxidized biologically more completely than was done chemically.

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TOD of glucose was obtained according to the reaction.

$$C_2H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$
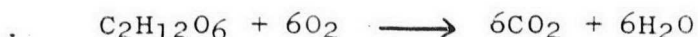
TOD thus calculated was compaired to BOD. The oxidation
efficiency of BOD to TOD was 34.6%.

This value is in agreement with that reported else-
where.

Aniline

COD and BOD_5 of aniline of various concentrations are given
in Table 3-2 and Fig. 3-2. The seed solution for this
experiment was taken from the activated sludge system,
which had such parameters that MLSS = 1,452 ppm and treat-
ment efficiency = 83.6%.

This result exhibited that aniline was not oxidized bio-
logically with the seed obtained from an usual activated
sludge system. In other words, the biological phase in
the usual activated sludge system was not acclimated enough
to oxidize aniline. In order to conform this result, the
various seeds taken from the activated sludge system
cultured under different conditions were used.

BOD_5 for any seeds was proved to be zero as shown in Table
3-3 and Fig. 3-3.

The glucose, which was examined under the same conditions
for the purpose of comparison, showed the appropriate value
of BOD.

In the preparative experiments, BOD test for a longer period exhibited the possibility of oxidation of aniline. Results was not given in this paper.

The oxidation efficiency was calculated. TOD of aniline was derived from the reaction

$$C_6H_5NH_2 + 7O_2 \longrightarrow 6CO_2 + 2H_2O + NH_3$$
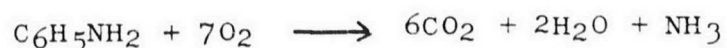
The value of TOD for aniline was 2.41 (g O_2/g aniline). The following results were deduced by using this value. Chemical oxidation efficiency of aniline with respect to TOD.

$$\frac{(COD/g \text{ aniline})}{(TOD/g \text{ aniline})} \times 100 = 86.7\%$$

Biological oxidation efficiency of aniline in refer to TOD.

$$\frac{(BOD/g \cdot aniline)}{(TOD/g \cdot aniline)} \times 100 = 0 \sim 5.7\%$$

On the other hand, the biological oxidation efficiencies of glucose with respect to TOD under the same conditions were about 21 to 44%.

Toiylene diisocyanate (TDI)

As already mentioned in the preceding chapter, TDI was easily hydrolyzed with water. The reaction products were mainly amines and polyureas.

In the present experiment, TDI was dissolved into water

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for a certain period at first. Then, the solution contain-
ing the products coming from hydrolysis of TDI was used as
a test sample.

First, COD for the filtrated solution in which hydrolysis
had proceeded for a certain period at room temperature
was measured.

The solution including TDI of 24,300 ppm was stored at
room temperature. After a certain period, the solution
was filtrated to remove suspended solid and COD was measured.
Tables 3-4 and 3-5 present the results for different
hydrolysis durations. COD for one gram of TDI added to
water is also given. The efficiency of chemical
oxidation in refer to TOD was calculated and given in
Tables 3-4 and 3-5.

TOD of TDI was derived according to the reaction.

$$C_9H_6N_2O_2 + 8O_2 \longrightarrow 9CO_2 + 2NH_3$$

Then,

$$TOD = 1.47 \ (g \ O_2/g \ TDI)$$

The value of efficiency for chemical oxidation
was as low as 0.1%.

On the other hand, as shown in Table 3-6 COD of the solution,
which was not filtrated and included suspended matters such
as polyurea, was as high as 0.6 to 0.8 g O_2/g TDI.

The efficiency of chemical oxidation to TOD for this solution

as high as 43 to 55 %.

Thus, the filtrated solution or supernatant after the
hydrolysis of TDI did not include the organic compounds
of high concentrations.   In other words, TDI was hydrolyzed
and was changed almost into the suspended solid matters
such as polyurea.

Second, BOD was measured for the hydrolyzed TDI.   The
sample solutions were not filtrated. The seed was also
taken from the activated sludge system, which was at the
conditions of MLSS = 2,428 ppm, SVI = 69.2.   The results
is given in Table 3-6 and Fig. 3-4.

The efficiency of biological oxidation in reference to
TOD of added TDI was also calculated to show in Table 3-6
and Fig. 3-5.   The efficiency was as low as 1 - 2%.

The numbers appearing in Fig.'s 3-4 and 3-5 are in accord-
ance with those in Table 3-6.

The comparison among No. 1, 2, and 3 in Table 3-6 indicates
that the time of hydrolysis does not give effect on the
BOD_5 and oxidation efficiency.

The oxidation efficiency decreased with the concentration
of added TDI.

The same kind of experiment on BOD with seed different from
the above experiment was conducted.

The result is given in Table 3-7 and Fig. 3-6.   In this

case BOD_5 was always nil and BOD_{10} was as low as 2 - 3

$(mg\ O_2/\ )$.

These results suggested that the susceptibility of bio-
logical oxidation for hydrolyzed TDI solution was dependent
on the biological phase of the seed. The comparison
between BOD_5 and BOD_{10} in Table 3-7 exhibited the accli-
mation of biological phase to hydrolyzed TDI solution
because the longer culture in the vessel gave the value
higher than zero.

Triethylene diamine (TED)

COD of triethylene diamine was measured to show in Table
3-8.

TED dissolved into water without appearent reaction. The
efficiency of chemical oxidation (COD) in refer to TOD was
calculated as given in Fig. 3-6. TOD was calculated according
to the reaction

$$C_6H_2N_2 + (15/2)\ O_2 \longrightarrow 6CO_2 + 3H_2O + NH_3$$

$$TOD = 2.14\ (g\ O_2/g\ TED)$$

The value of COD was ranged between 65 and 85%.
This indicated that TED was not decomposable in the water
and accepted chemical oxidation easily.
On the other hand, BOD_5 test exhibited that the difficulty
in biological oxidation of TED as shown in Table 3-9 and
Fig. 3-7.

The seed used for the BOD test was also taken from the activated sludge system described previous chapters. The biological oxidation of glucose conducted with the same seed for the purpose of comparison gave the reasonable value as shown in Table 3-9.

3.4 Conclusion

Being based upon the results obtained from COD and BOD measurements, the followings were calculated.

1) Corn steep liquor with which the activated sludge system in the present experiment was acclimated was highly oxidizable in the biological manner. BOD_5 and COD gave the excellent proportionality.

The efficiency of biological oxidation was as twice as that of chemical oxidation.

2) Glucose was also oxidized easily with any seeds taken from the activated sludge system in the present use.

3) Aniline accepted the chemical oxidation with an efficiency of 86.7% in reference to TOD.

However, it was slightly oxidized biologically within 5 days for any seeds taken from the activated sludge system in the present experiment.

4) Tolylene diisocyanate reacted rapidly with water to give white suspended matter. The filtrated solution of the above suspension gave the very low value of COD.

On the contrary, COD of the suspension was high. The former oxidation efficiency in reference to TOD was as low as 0.1%, while the latter was 43 to 55%. COD of filtrated solution stayed at a low value for the hydration duration longer than 50 minutes.

5) Suspension obtained from the hydrolysis of tolylene diisocyanate gave low value of BOD_5. This was due to the difficulty in biological oxidation of the suspended matters. It was observed that the biological phase could be acclimated with this suspension.

6) The aqueous solution of triethylene diamine was subject to chemical oxidation with an efficiency of 65 to 85% in reference to its TOD. However, it was not oxidized biologically within 5 days.

3.5 Useful Informations and Suggestions Abstructed

1) Aniline, tolylene diisocyanate and triethylene diamine were not able to be oxidized with the biological phases acclimated with domestic waste waters within a short period. However, acclimation of biological phase with aniline and hydrolyzed solution of tolylene diisocyanate would be possible.

2) Tolylene diisocyanate reacted rapidly with water to give white suspended matters.

Thus, the removal of tolylene diisocyanate by hydrolysis
would be promising.

The suspension after hydrolysis gave a BOD value larger
than zero.

Thus, the complete reaction of TDI with water would
minimize the water pollution as long as the appropriate
consideration is paid.

3) COD for corn steep liquor which is the substrate of
the activated sludge used in the present experiment is
a satisfactory substitute of BOD_5 for it.

Table.3-1. COD AND BODs OF CSL AND GLUCOSE

Sample	COD	BOD$_5$
Effluent	30.9	13.8
CSL 1.	94.4	223
2.	182	428
3.	272	599
4.	336	635
Glucose	188	111

Table. 3-2. COD AND BOD₅ OF ANILINE AND GLUCOSE

Concentra-tion of sample $\times 10^{-4}$ %	COD	BOD$_5$
ANILINE		
4.08	8.20	O
10.2	20.5	O
20.4	41.0	O
40.8	82.0	5.4
102	205	O
GLUCOSE		
300	188	140

Table.3-3. BOD₅ OF ANILINE FOR VARIOUS SEEDS

Seed in various conditions	BOD_5 $[mgO_2 \, l^{-1}]$
Mixed liquor of activated sludge cultured with only tap water	0
Mixed liquor of activated sludge, 15 minutes after feeding C S L	0
Mixed liquor of activated sludge, 60 minutes after feeding .C S L	0
Supernatant of activated sludge, 120 minutes after feeding C S L	0
Supernatant of activated sludge, 240 minutes after feeding C S L	0

Glucose   as   refernce

Supernatant of activated sludge, 180 minutes after feeding CSL	67.5

Table 3-4. COD OF FILTERED SOLUTIONS OF TDI HYDROLYZED FOR VARIOUS PERIODS AND OXIDATION EFFICIENCY TO TOD

Time after preparation [min]	COD		Oxidation efficiency [%]
	$mg\,O_2/l$	$g\,O_2/g\,TDI$	
50	0	0	0
80	53.0	2.18×10^{-3}	0.148
110	53.2	2.19×10^{-3}	0.149
140	44.7	1.84×10^{-3}	0.125

Table. 3-5. COD OF FILTERED SOLUTION OF TDI
HYDROLYZED FOR VARIOUS PERIODS
TO OXIDATION EFFICIENCY TO TOD

Time after preparation [day]	COD		Oxidation efficiency [%]
	mg O_2/L	gO_2/g TDI	
28	54.0	2.22×10^{-3}	0.151
8	403	1.66×10^{-2}	1.13
7	163	6.71×10^{-3}	0.456
6	39.7	1.63×10^{-3}	0.111
5	0	0	0
1	255	1.05×10^{-2}	0.714

Table. 3-6. CHEMICAL AND BIOLOGICAL OXIDATION OF HYDROLYZED TDI

Sample No.	Dilution ratio of added TDI in terms of volume per volume ppm	Keeping time after preparing sample days	C O D		Oxidatin efficiency of COD to TOD %	B O D$_5$		Oxidation efficiency of BOD$_5$ to TOD %
			$\frac{mgO_2}{l}$	$\frac{gC_2}{gTDI}$		$\frac{mgO_2}{l}$	$\frac{gO_2}{gTDI}$	
1	100	7	76.3	0.625	42.5	3.9	0.032	2.2
2	100	1	97.9	0.802	54.6	1.8	0.015	1.0
3	100	0				3.2	0.026	1.6
4	300	0				5.2	0.016	1.1
5	600	0				6.0	0.0018	0.67
Glucose solution as ref.	$3 \times 10^{-4} \left[\frac{g\ Glucose}{g\ Solution} \right]$	0	188	0.626	58.5	142	0.474	44.3

Table 5-7. BOD5 AND BOD10 OF TDI

Concentration of sample [ppm]	BOD5		Oxidation efficiency [%]
	mgO₂/L	gO₂/g-TDI	
120	0	0	0
720	0	0	0

Reference

Glucose 300	144	0.480	44.9

Concentration of sample [ppm]	BOD10		Oxidation efficiency [%]
	mgO₂/L	gO₂/g-TDI	
120	2	0.0017	0.12
720	3	0.0042	0.28

Reference

Glucose 300	230	0.767	71.7

Table 3-8. COD OF TED SOLUTION AND OXIDATION EFFICIENCY TO TOD

Concentration of TED [ppm]	COD		Oxidation efficiency [%]
	mg O_2/l	g O_2/g TED	
85.2	118	1.38	64.5
152	187	1.23	57.5
94.0	170	1.81	84.6

Table 3-9. BODs OF TED AND OXIDATION EFFICIENCY TO TOD

Concentration of TED [PPM]	BODs		Oxidation efficiency [%]
	mg O₂/l	gO₂/g TED	
290	0	0	0
570	0	0	0
1150	0	0	0
2000	0	0	0
2870	0	0	0

Reference

Glucose 300	165	0.550 gO₂/g Glucose	51.4
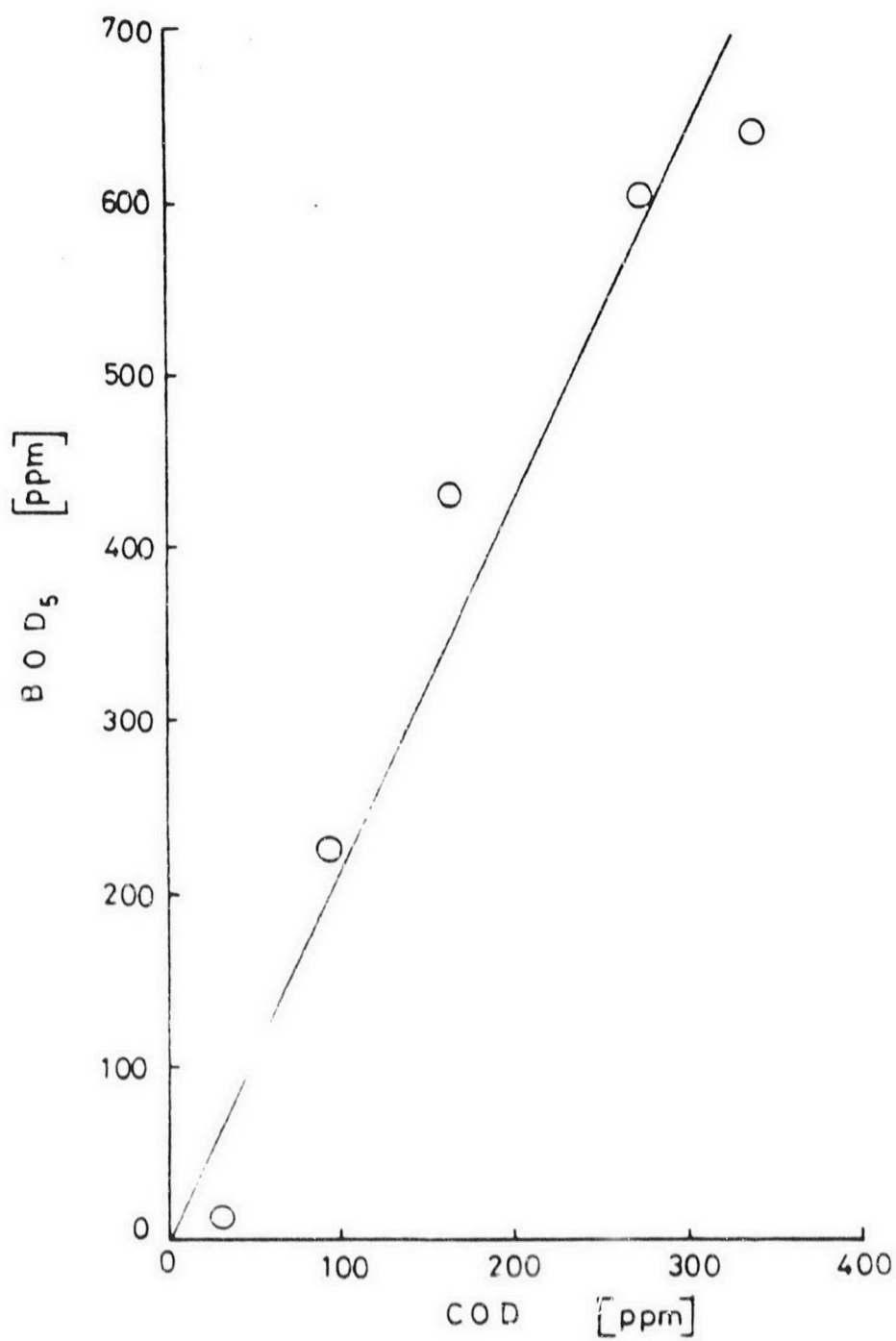
Fig. 3-1. RELATION BETWEEN BOD₅ AND COD FOR CORN STEEP LIQUOR
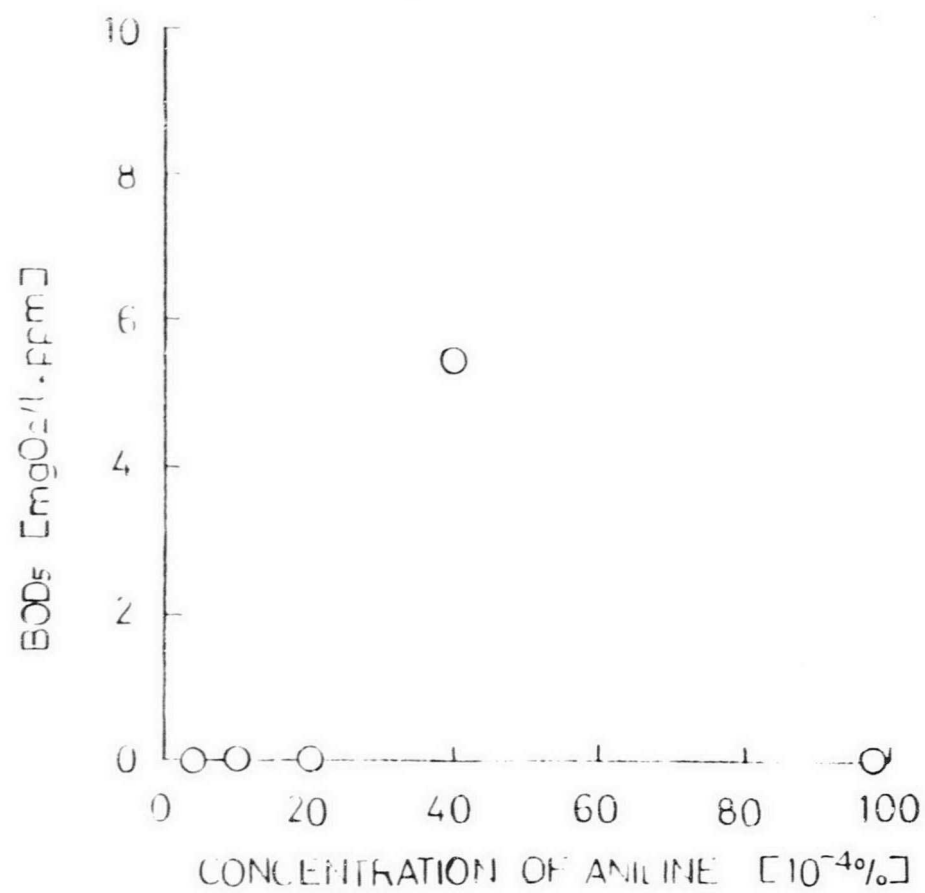
Fig. 3-2. BOD₅ OF ANILINE
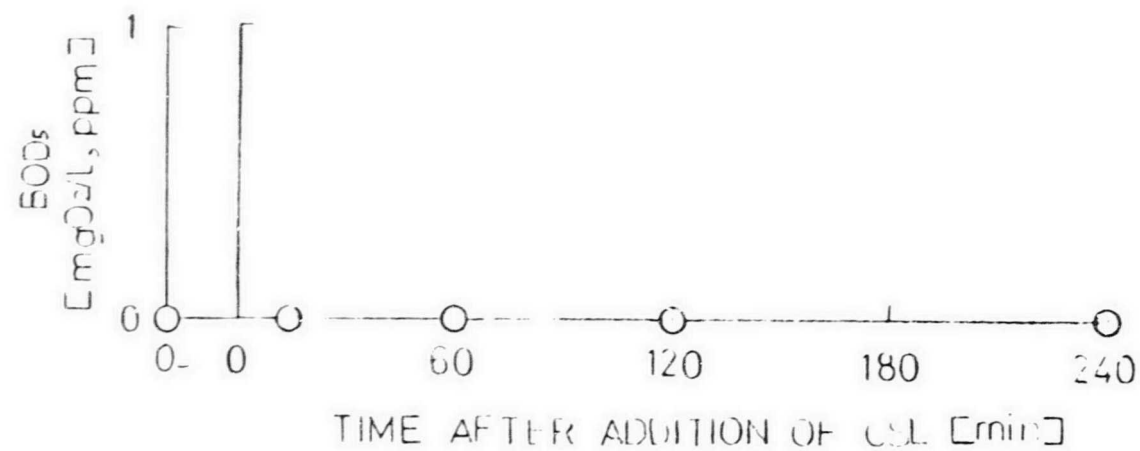
Fig. 3-3. BODs OF ANILINE WITH SEEDS TAKEN FROM ACTIVATED SLUDGE SOLUTION CULTURED WITH CSL
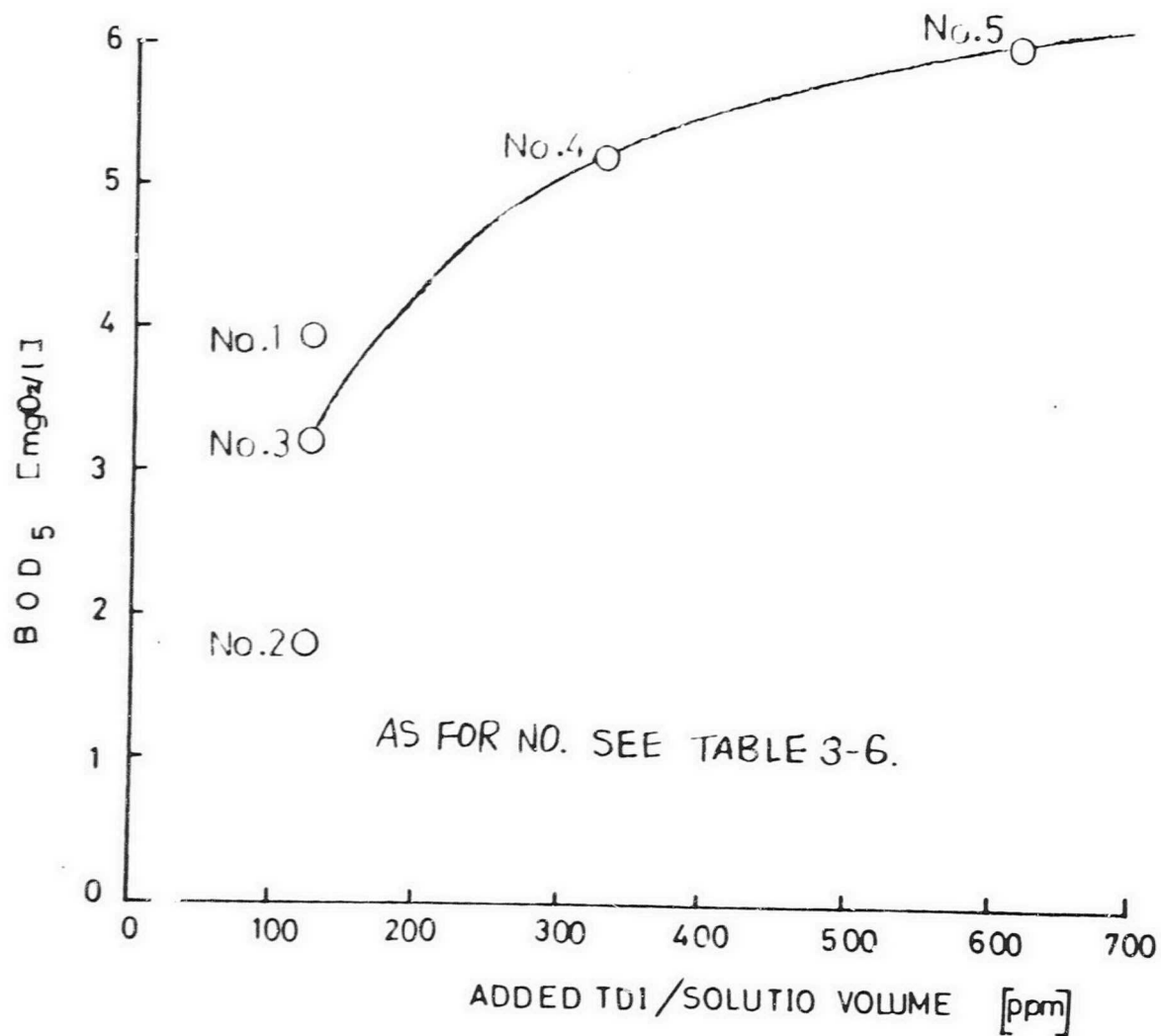
Fig. 3-4. BOD$_5$ OF HYDROLYZED TDI
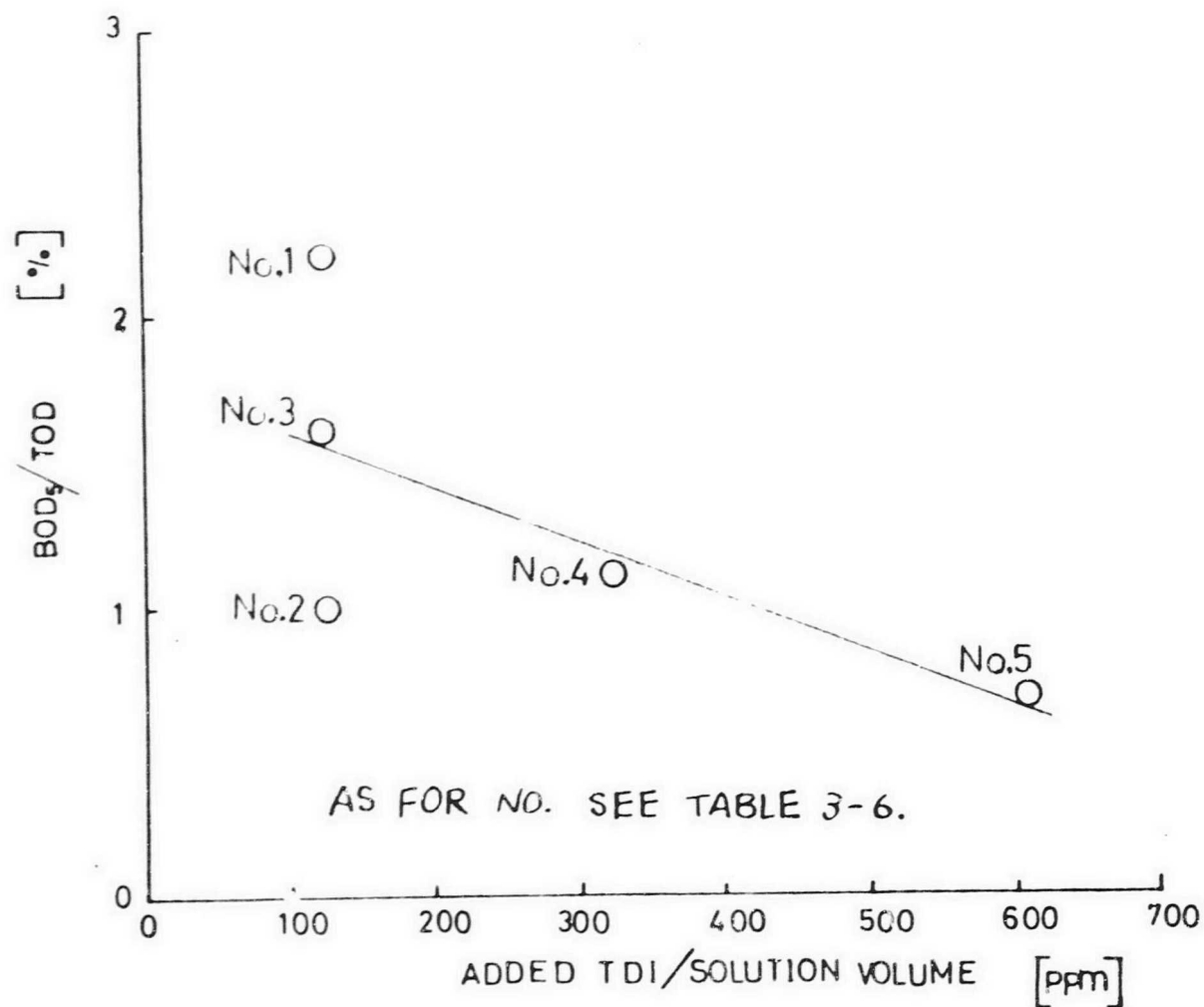
Fig. 3-5. BIOLOGICAL OXIDATION EFFICIENCY OF TDI
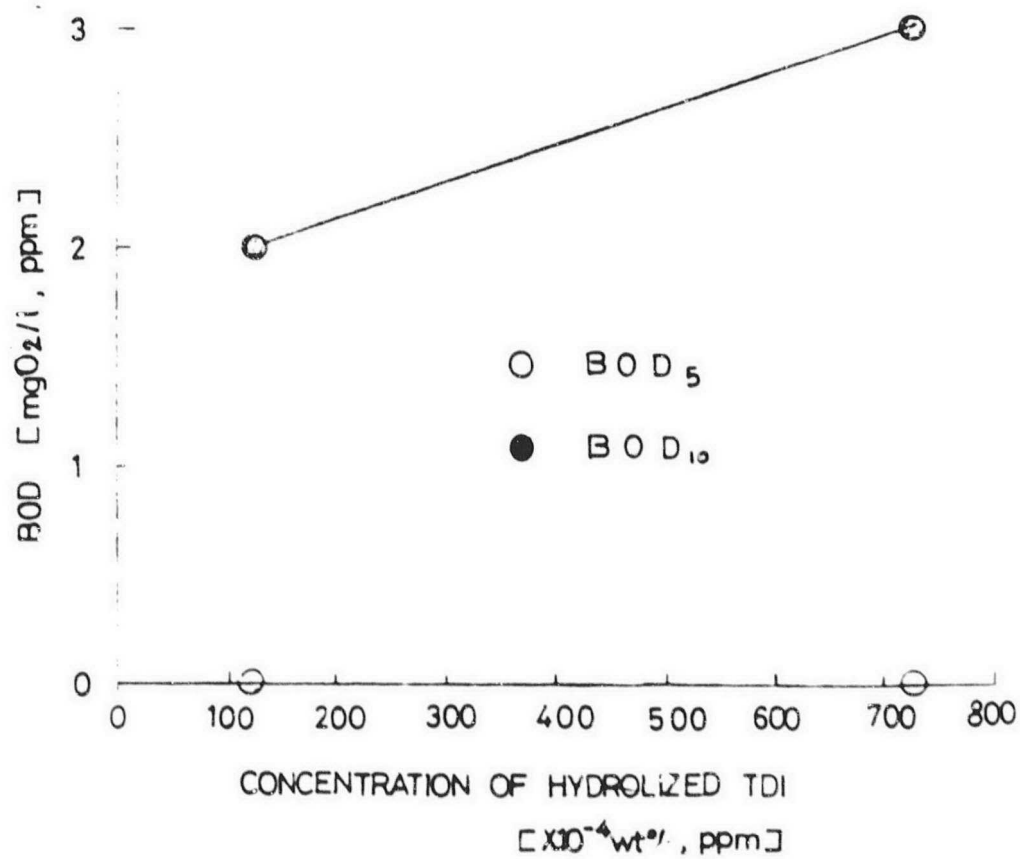
Fig. 3-6. BODs AND BODi₀ OF HYDROLYZED TDI
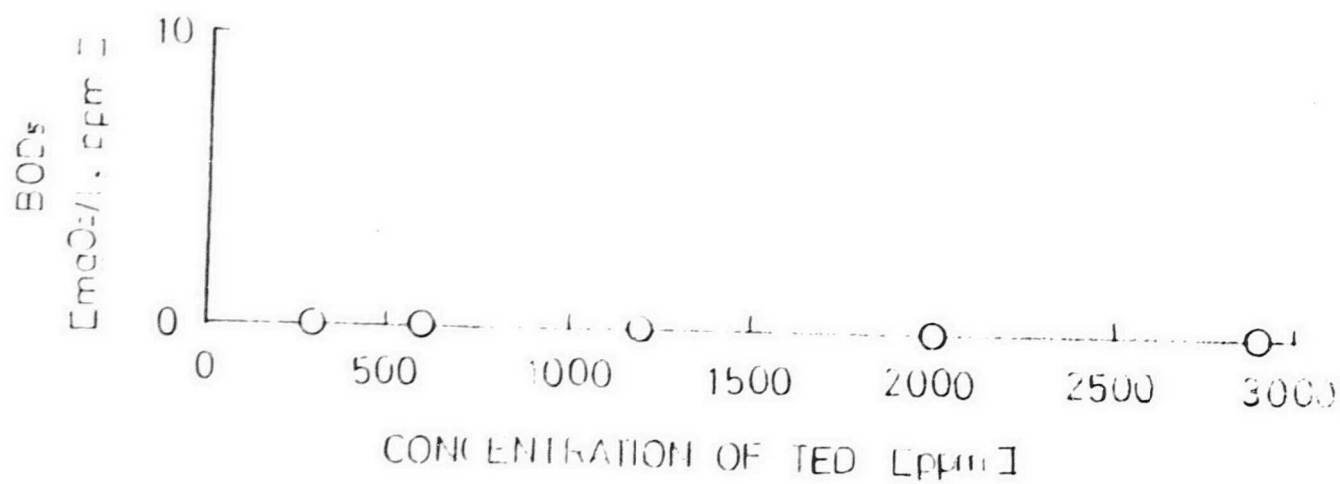
Fig. 3-7. BODs OF TED

4. Response of Activated Sludge to Addition of Aniline

4.1 Introduction

As described in the earlier chapter in this report, tolylene diisocyanate reacts with water to give a variety of amines and polyureas. Thus, in order to find the impact of matters produced via. the hydration of TDI on aqua-ecosystem, the effect of amines should be investigated.

In this chapter, the biological effect of aniline, which is the simplest amine, on the activated sludge system is described.

The biological activity of the activated sludge system (ASS) was evaluated by measuring the respiration rates. This evaluation was employed on the basis that activated sludge system degradated substrates by consuming oxygen. The aim of this chapter is to prepare the informations with which the results in the latter chapters would be compared.

4.2 Experimental

Activated sludge solutions of 200 to 250 ml taken from the culture vessels described in the earlier chapter were introduced into the measurement vessel shown in Fig. 4.1. The temperature of measurement vessel was maintained at

$25 \pm 1^\circ C$.

Dissolved Oxygen concentration (DO) and pH were measured and recorded simultaneously.

The solution was aerated at first and DO was increased up to 7 to 8 mg/L.

Then, the aeration was stopped and decrease in DO was recorded, DO decreased linearly with time down to 1 mg/L. In the course of deaerated process, an additive (aniline solution) was added. During the above process, the solution was kept stirring.

The illustrative changes of DO are given in Fig. 4-2 and 4-3.

Respiration rates were obtained from the slope of decreasing DO. The respiration rates before addition of an additive and after its addition were represented by $r.r._1$ and $r.r._2$.

It was found that the difference in volume of sampled solution did not alter the respiration rates.

Aniline was diluted with water by 5 and 20 times. Aniline solutions diluted and undiluted were used. The quantity of added aniline was a few ml.

4.3 Results

4.3.0 The number of tables and figures

In this chapter, a few experimental data should be given

as a set.

Accordingly, the numbers of tables and figures were given in a special way. The independent tables and figures were numbered in the same way as preceding chapters.

Table 4 · 3

Fig. 4 · 5

Number in chapter 4.
Representing the chapter

A set of tables and figures were given in the following way.

4 5

Number of chapter

Set number for experiment

Number of table or figure
in the set
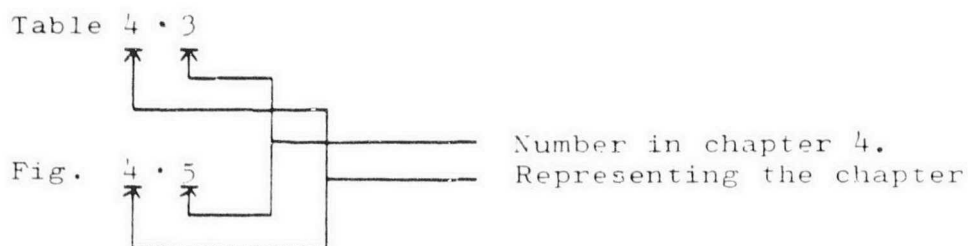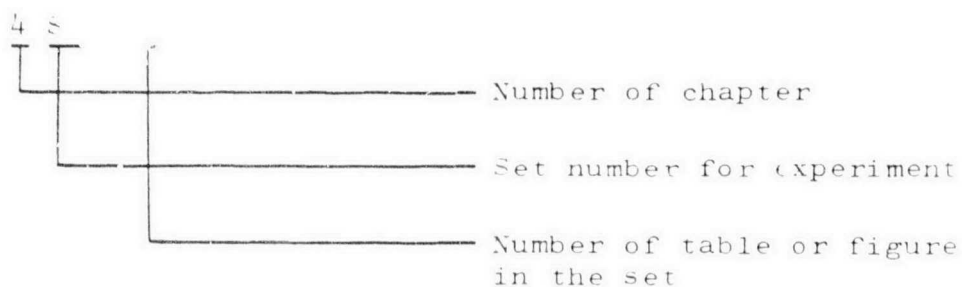
The tables for X = 0 such as 4S5-0, 4S7-0, give the data on the activated sludge used for the set of experiments. The data on the culture of activated sludge for tank number IV can be found in Chapter 2 in this report.

4.3.1 Change in respiration rate of various activated sludges with addition of aniline

The activated sludges of various characters were prepared with different cultures. The characters were listed in Tables of 4SY-0, where Y (= 1, 2, ...) represented experimental set number.

The concentration of aniline in the measurement vessels and respiration rates were given in Tables 4SY-1.

The concentration was calculated in terms of weight. Respiration rates were expressed with respect to the unit quantity of MLSS.

Then, the dimension of respiration rate was $mg(O_2) \cdot hr^{-1} \cdot g^{-1}(MLSS)$. In Tables 4SY-1, the loading rate with respect to MLSS and the ratio of the respiration rate after the addition of aniline (r_2) to that before the addition (r_1) are given.

$r.r._2/r.r._1$ may be a measure of the impact which the addition of aniline gives. When $r.r._2/r.r._1 > 1$ the respiration rate was accelerated by addition of aniline and vice versa.

In the experimental sets from 4S1-X to 4S7-X, the activated sludges were cultured with continuous feeding of corn steep liquor. Figures 4SY-1 (Y = 1 to 7) give the dependence of $r.r._2/r.r._1$ on the loading rate of aniline. In any figure,

$r.r._2/r.r._1$ has a minimum and a maximum.

The minimum appeared in the range of loading rate between 0.4 and 0.8 $g(\text{aniline}) \cdot hr^{-1} \cdot g^{-1}(\text{MLSS})$ and its value was always less than 1.

The maximum was observed for the loading rate around 2 $g(\text{aniline}) \cdot hr^{-1} g^{-1}(\text{MLSS})$ and its value was larger than 1. This indicated that aniline acted as an inhibitor to the respiration activity at the very low and very high loading rates, while it accelerated the respiration rate at the intermediate loading rates.

In the experiments of 4S8-X and 4S9-X, the activated sludge had been aerated without feeding corn steep liquor for a day or more.

In these cases, $r.r._2/r.r._1$ was almost less than 1 and did not give maximum nor minimum.

In other words, aniline behaved as an inhibitor for the activated sludge aerated without feeding for a period.

4.3.2 <u>The relation of $r.r._2/r.r._1$ with $r.r._1$ for the activated sludge whose state changed continuously</u>

In order to find the relation of $r.r._2 \, r.r._1$ with respiration activity of the activated sludge, $r.r._2/r.r._1$ was measured for the activation sludge whose respiration rate changed continuously. The experimental procedure was as follows. The activated sludge solutions (about 10 L.)

which had been cultured with continuous feeding of corn steep liquor was taken from the culture vessel. Then, the solution was aerated without feeding the substrates for a day or more until the respiration rate became low enough. After the respiration mode of activated sludge was evident to be endogenous, the corn steep luquor of an amount was added.

The change in pH with time after the addition of CSL is given in the Figures 4SY-1 (Y = 10 and 12).

After pH attained a minimum value, it was recovered again. Figures 4SY-2 (Y = 10, 11, 12) exhibit the change of respiration rate before addition of aniline $(r.r._1)$ with time. It decreased monotonously and attained a steady value.

The effect of aniline was investigated for the activated sludge after the addition of corn steep liquor. The activated sludges were taken at various time after the addition of corn steep liquor and were subject to the experiments of addition of aniline. The amounts of aniline added to the activated sludges were 1.06, 2.00, and 3.16 g/g MLSS for the experiments 4S10-X, 4S11-X, and 4S12-X, respectively.

Figures 4SY-3 (Y = 10, 11, and 12) give the change of $r.r._2/r.r._1$ with time after the addition corn steep liquor.

The definite tendency was not observed. In Figures 4SY-4 $(Y = 10, 11,$ and $12)$, $r.r._2/r.r._1$ is plotted against $r.r._1$. When the loading rate of aniline was low (experiment 4S10-X), the definite tendency such as $r.r._2/r.r._1$ decreased with increase in $r.r._1$ was obtained. However, this tendency did not appear for the high loading rate of aniline (experiments 4S11-X and 4S12-X).

This relation indicated that aniline inhibited the respi-- ration activity when it was high while aniline stimulated the respiration activity when it was low. Further more, it would be suggested that aniline acted as a substrate when another substrate was short while it acted as an inhibitor when another substrate existed enough.

4.3.3. <u>Response of over loaded activated sludge to the addition of aniline</u>

A relatively large amount of corn steep liquor was feeded to the activated sludge system. The activated sludge thus cultured was taken and aerated without feeding. Accordingly, the experiment 4S13-X was done.

pH increased monotoneously and $r.r._1$ decreased in the same manner as appearing in Figures 4S13-1 and 4S13-2. The experiment of addition of aniline was done for the acti- vated sludges under various conditions during aeration without feeding.

$r.r._2/r.r._1$ against time after the release from over-loaded cultivation was plotted in Figure 4S13-3. The plot of $r.r._2/r.r._1$ against $r.r._1$ was also examined in Figure 4S13-4. Both figures did not present any a definite relation except that $r.r._2/r.r._1 < 1$.

4.4   Discussions

1) The activated sludges cultured continuously would be similar to the actual plant of biological waste water treatment.

For the activated sludge of this kind, aniline could be a substrates if the aniline concentration and biological phase are appropriate because $r.r._2/r.r._1$ exceeded unity

The activated sludge cultured under over-loaded conditions could never be activated by aniline. When the concentration of aniline is excessively high, aniline acts as an inhibitor.

2) A comparison between biological phase and the value of $r.r._2/r.r._1$ was carried out.

In Table 4.7, the value of $r.r./r.r.$ was compared with the existence or absence of vorticella through whole experiments. In the activated sludge where

vorticella was found $r.r._2/r.r._1$ exceeded unity at some
concentration of aniline and vice versa.

4.5   Conclusion

1) Aniline could act both as a substrate and as an inhibitor
in the activated sludge.

2) In the activated sludge cultured continuously under
appropriate conditions, aniline behave like a substrate
in some concentration range i.e. approximately 1 - 2
g/g(MLSS).

3) In the activated sludge cultured under over-loaded
conditions, aniline always inhibited the respiration
activity.

4) When the concentration of aniline was not very high,
$r.r._2/r.r._1$ was corelated with $r.r._1$. In the case
where $r.r._1$ was low $r.r._2/r.r._1$ exceeded unity and
acted as a substrate, and vice versa.

5) The biological phase was found to be closely related
to the effect of aniline. In the activated sludge in
which vorticella was found aniline could be a substrate.

4.6   Useful Informations and Suggestions Abstructed

1) Aniline could not be harmful to the activated sludge of
waste water treatment plant for domestic use when the
dilution of aniline is appropriate.

- 157 -

2) If the activated sludge system is acclimated properly,
   the biological treatment of aniline seems to be possible.

3) The possibility of the biological treatment of aniline
   can be determined from the biological phase.

TABLE 4.1
DEPENDENCE OF RESPIRATION ACTIVITY ON BIOLOGICAL PHASE (VORTICELLA)

EXPERIMENT NUMBER	VORTICELLA	$\left(\dfrac{R.R.2}{R.R.1}\right)_{max}$
4S1-X	NOT FOUND	≤ 1
4S2-X	FOUND	> 1
4S3-X	FOUND	> 1
4S4-X	FOUND	> 1
4S5-X	FOUND	> 1
4S6-X	FOUND	> 1
4S7-X	FOUND	> 1
4S8-X	NOT FOUND	≤ 1 *
4S9-X	NOT FOUND	≤ 1
4S10-X	FOUND	> 1
4S11-X	NOT FOUND	≤ 1
4S12-X	NOT FOUND	≤ 1
4S13-X	NOT FOUND	≤ 1

* A few exceptions for very low concentration of aniline.
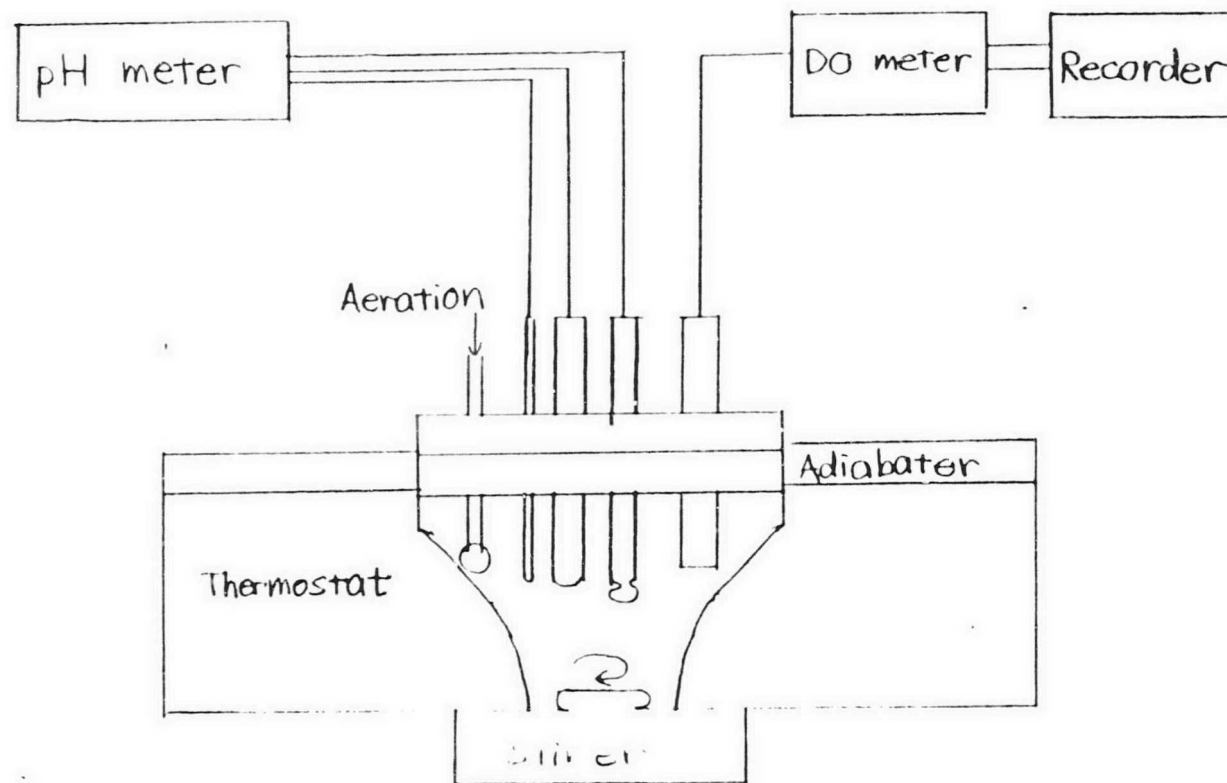
Fig. 4.1. EQUIPMENT FOR MEASUREMENT OF RESPIRATION RATE
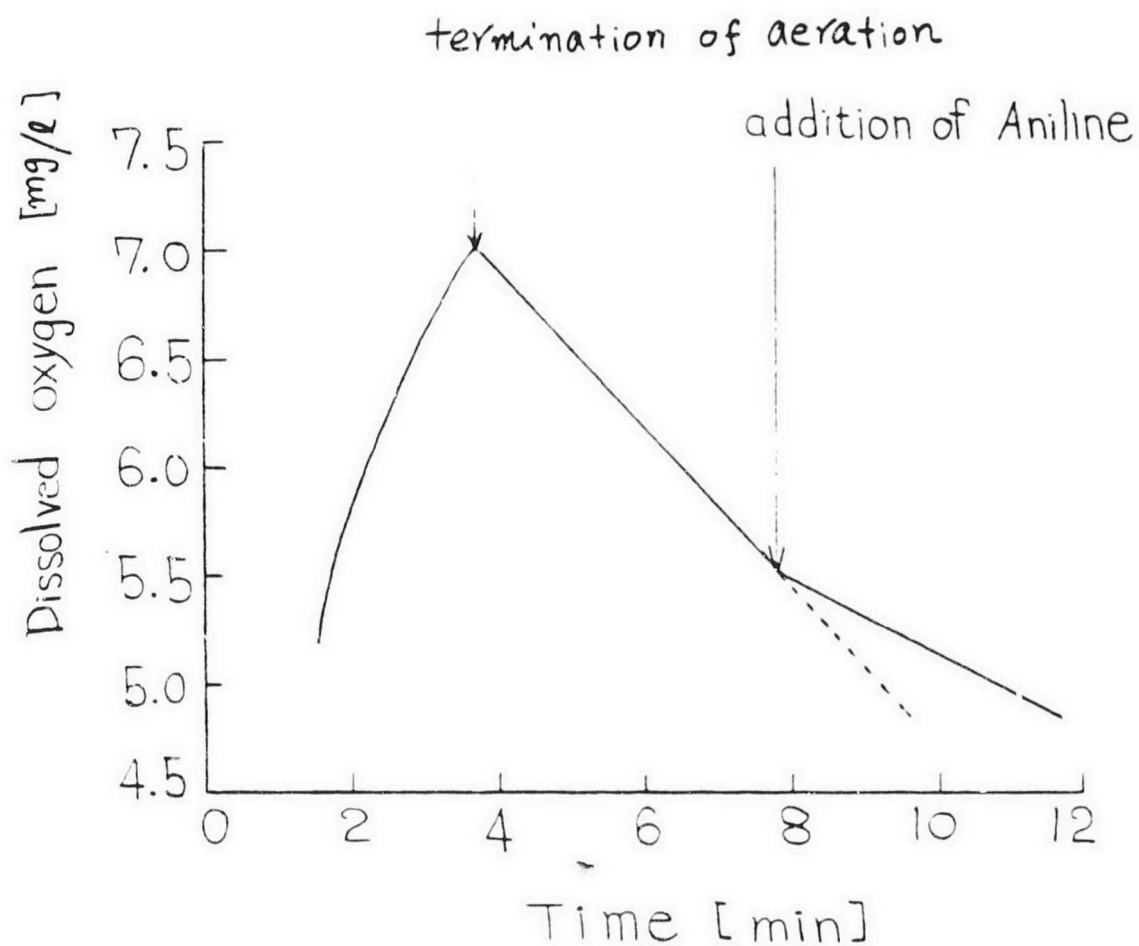
Fig 4.2 CHANGE IN DO ($r.r._1 > r.r._2$)

Fig4.3. CHANGE IN DO $(r.r._1 < r.r._2)$

4S1-0

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON-CENTRATION (mg/l) D O		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2242	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	15.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	66.9	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT
Vorticella was not found.

TABLE 4S1-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge gAniline/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
810	0.361	4.98	2.09	0.42
1620	0.723	4.23	2.14	0.51
2430	1.08	2.41	1.71	0.71
2030	0.905	3.48	1.98	0.57
1220	0.544	3.43	1.61	0.47
410	0.183	3.38	1.07	0.32
810	0.361	2.95	0.803	0.27
1620	0.723	3.15	1.50	0.48
2430	1.08	2.90	2.90	1.00

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ------ RESPIRATION RATE AFTER LOADING

Fig. 4. S. 1-1   EFFECT OF ANILINE ON RESPIRATION RATE
OF CONTINUOUSLY CULTURED ACTIVATED SLUDGE

4S2-0

DATE 10/25

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	22.4	pH	6.5
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.4	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2848	INFLUENT COD(mg/l) COD_{in}	20.9
SPECIFIC VOLUME SV_{30}	16.5	EFFLUENT COD (mg/l) COD_{eff}	11.1
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	57.9	REMOVAL EFFICIENCY OF COD (%)	92.2
INFLUENT WATER FLOW RATE (l/day)	212	FOOD:MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	0.047
HYDRAULIC DETENTION TIME (hr^{-1})	11.1	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 4S2-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM   (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge g Aniline/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
4060	1.43	3.55	4.23	1.19
8090	2.84	2.95	3.38	1.14
2040	0.716	4.35	2.60	0.60
6080	2.13	3.35	4.23	1.28
4060	1.43	3.80	3.70	0.98
4060	1.43	3.03	3.63	1.19

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ------ RESPIRATION RATE AFTER LOADING
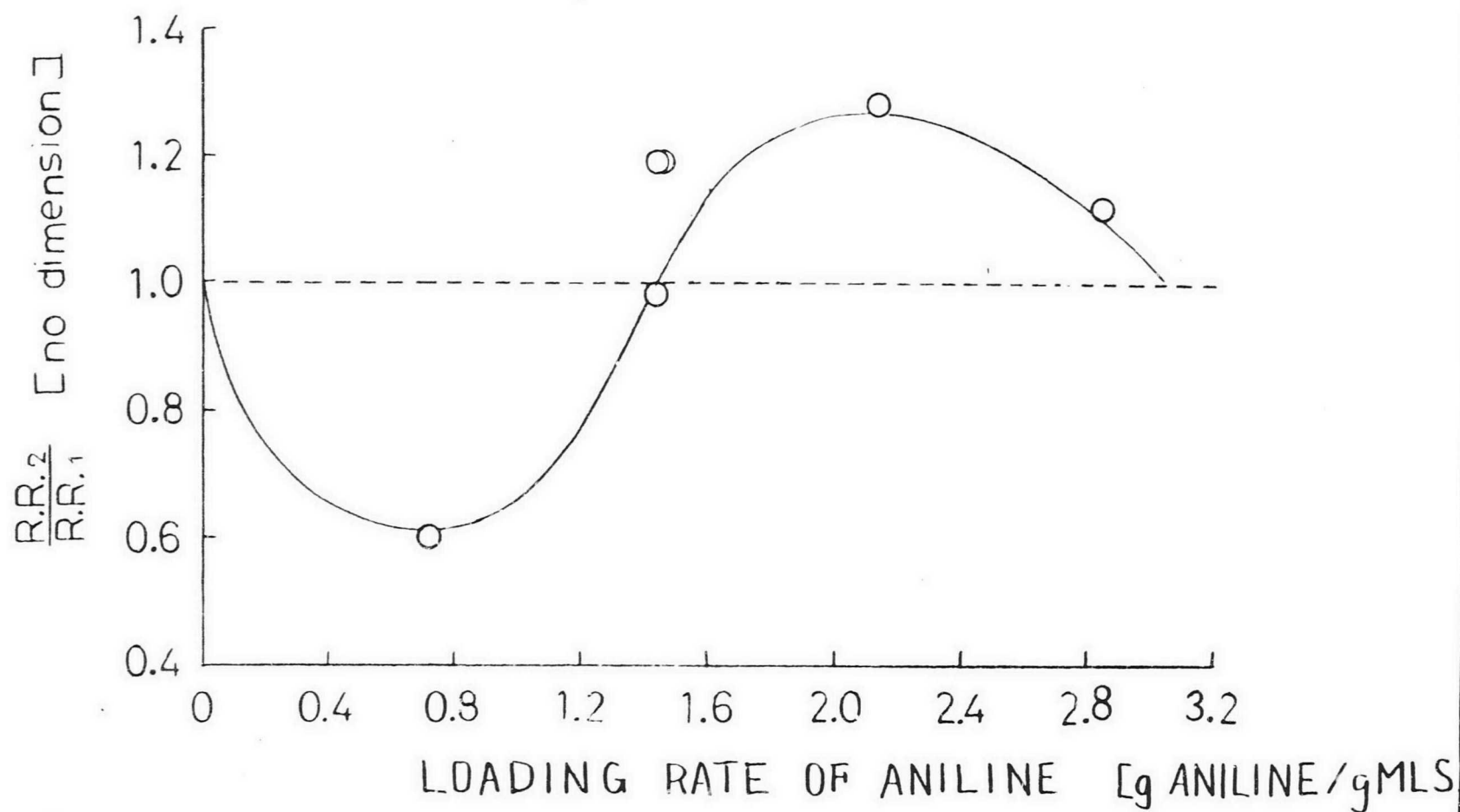
Fig. 4S2-1   EFFECT OF ANILINE ON RESPIRATION RATE

4S3-0

DATE 10/26

AERATION TANK No.	IV	LOADING CONDITION	(continu-ous)
TEMPERATURE (°C) T	23.2	pH	5.86
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO	0.6	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2580	INFLUENT COD(mg/l) COD_{in}	75.7
SPECIFIC VOLUME SV_{30}	14.0	EFFLUENT COD (mg/l) COD_{eff}	12.1
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	54.3	REMOVAL EFFICIENCY OF COD (%)	84.0
INFLUENT WATER FLOW RATE (l/day)	240	FOOD : MICROORGANISM RATIO F/M (gCOD / gMLSS·day)	0.072
HYDRAULIC DETENTION TIME (hr^{-1})	9.8	RESPIRATION RATE (mg O_2/ hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 4S3-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM ‾ ‾ (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge g Aniline/g MLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
4060	1.57	5.25	4.65	0.89
2040	0.791	5.13	3.83	0.75
4060	1.57	4.65	4.43	0.95
2040	0.791	3.95	3.30	0.84
2040	0.791	4.10	2.19	0.53
4060	1.57	3.73	3.73	1.00
3050	1.18	5.45	5.13	0.94
3050	1.18	4.83	4.48	0.92
4060	1.57	4.43	3.63	0.84
3050	1.18	3.95	3.13	0.79
3050	1.18	4.33	3.68	0.85
4060	1.57	4.48	3.58	0.80
2040	0.791	3.50	2.88	0.83
3050	1.18	2.93	3.58	1.22
1020	0.395	3.40	2.47	0.73
1020	0.395	3.40	2.09	0.62
1020	0.395	3.18	2.33	0.74

$r.r_1$ ······ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ······ RESPIRATION RATE AFTER LOADING

Fig. 4S3-1   EFFECT OF ANILINE ON RESPIRATION RATE OF CONTINUOUSLY CULTURED ACTIVATED SLUDGE

4S4-0

DATE 10/30

AERATION TANK No.	IV	LOADING CONDITION	Continuous
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2984	INFLUENT COD(mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	15.1	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	54.0	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)	238	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})	9.9	RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 484-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge g.Aniline/gMLSS	$r.r_1$ $\frac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.r_1}{r.r_2}$ no dimension
4060	1.36	9.55	9.55	1.00
6080	2.04	8.55	8.85	1.04
2040	0.684	8.45	8.45	1.00
820	0.275	7.65	6.03	0.79
5070	1.70	7.95	9.05	1.14
3250	1.09	7.15	8.05	1.13
8090	2.71	7.25	4.83	0.67
410	0.137	6.63	5.53	0.83
410	0.137	7.95	7.05	0.89
81	0.0271	7.45	6.63	0.89
1620	0.544	7.25	6.53	0.90
200	0.0670	7.45	6.03	0.81
100	0.0355	7.25	6.03	0.83
410	0.137	7.65	6.63	0.87

$r.r_1$ ······ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ······ RESPIRATION RATE AFTER LOADING
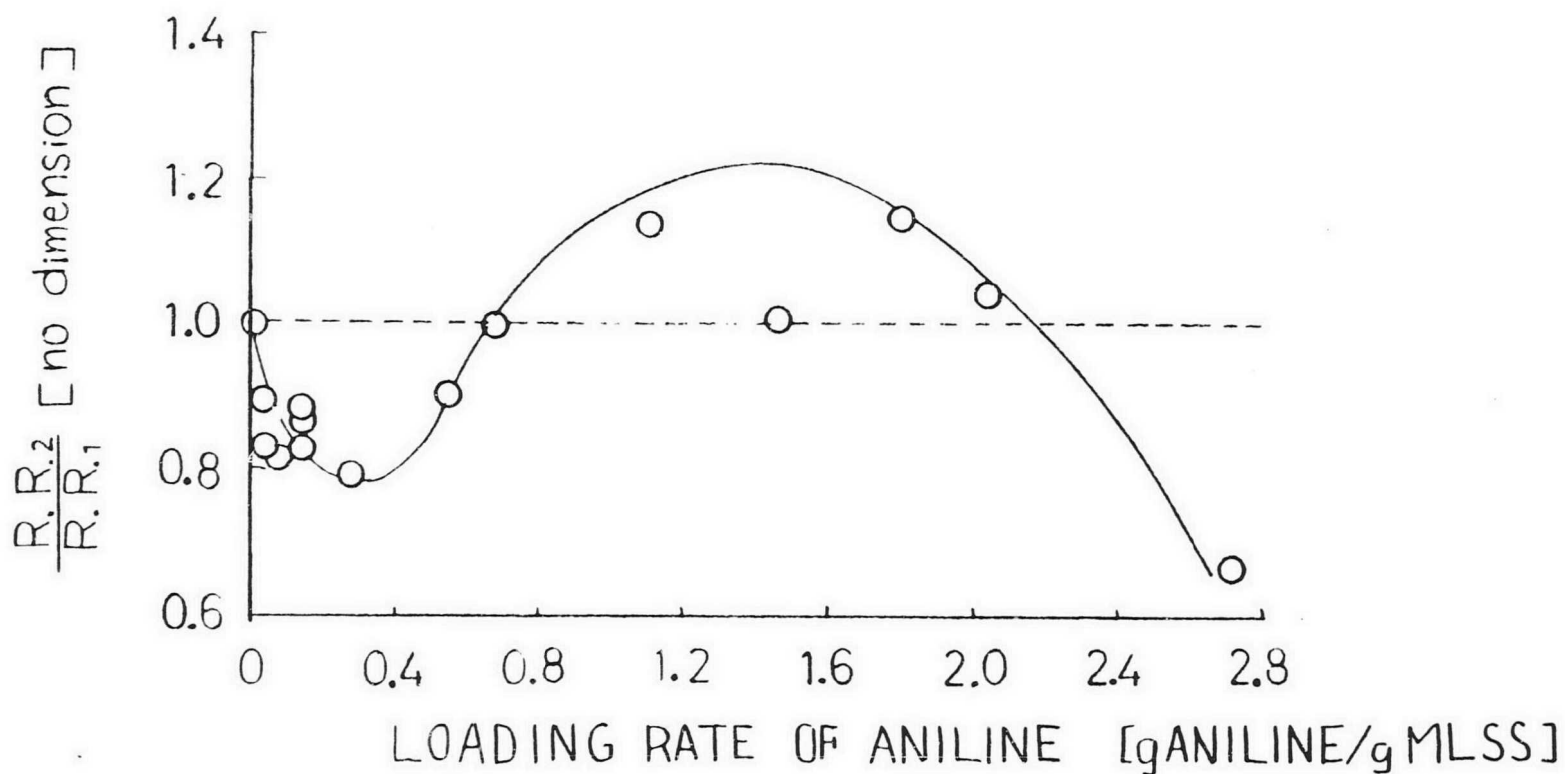
Fig. 4S4 - 1.   EFFECT OF ANILINE ON RESPIRATION RATE

4S5-0

DATE 11/2

AERATION TANK No.	IV	LOADING CONDITION	Continuous
TEMPERATURE (°C) T	24.0	pH	6.39
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO	0.6	OXIDATION-REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2992	INFLUENT COD (mg/l) COD_{in}	83.2
SPECIFIC VOLUME SV_{30}	18.6	EFFLUENT COD (mg/l) COD_{eff}	20.8
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	62.2	REMOVAL EFFICIENCY OF COD (%)	75.0
INFLUENT WATER FLOW RATE (l/day)	245	FOOD:MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	0.069
HYDRAULIC DETENTION TIME (hr^{-1})	9.6	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 4S5-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM ~ (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge $\frac{g\,Aniline}{g\,MLSS}$	$r.\,r_1$ $\frac{mgO_2}{hr\,gMLSS}$	$r.\,r_2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.\,r_1}{r.\,r_2}$ no dimension
4060	1.36	6.13	8.03	1.31
10	3.34×10^{-3}	5.46	5.63	0.97
2040	0.682	5.23	5.23	1.00
5	1.67×10^{-3}	5.03	4.83	0.96
5070	1.69	4.50	6.53	1.44
2	6.68×10^{-4}	4.73	4.73	1.00
8090	2.70	4.83	4.93	1.02
6080	2.03	4.60	6.03	1.30
50	0.0170	4.00	4.00	1.00
12100	4.04	4.00	1.30	0.33

$r.\,r_1$ ...... RESPIRATION RATE BEFORE LOADING

$r.\,r_2$ ...... RESPIRATION RATE AFTER LOADING
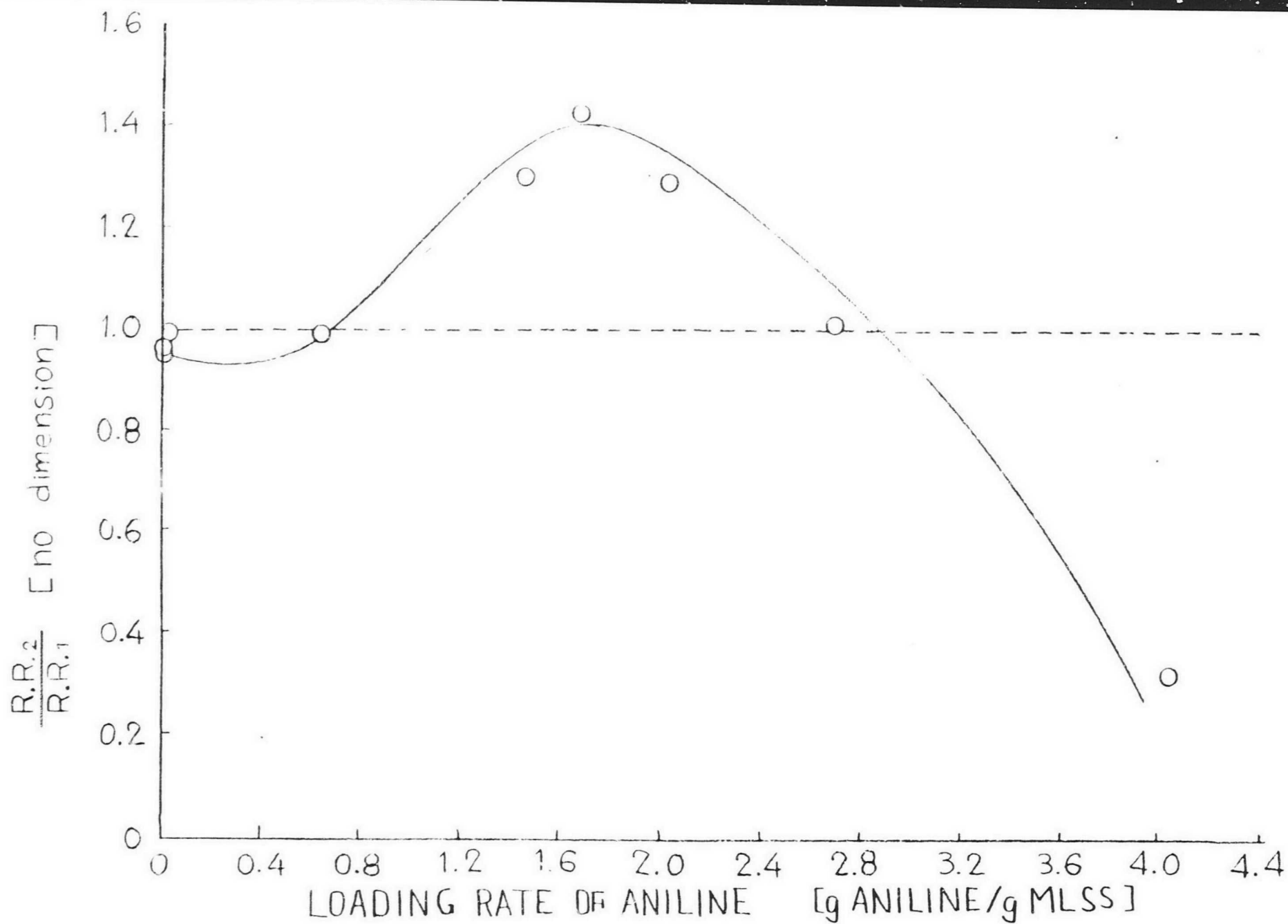
Fig. 4S5-1. EFFECT OF ANILINE ON RESPIRATION RATE OF CONTINUOUSLY CULTURED ACTIVATED SLUDGE

4S6-0

DATE 10/24

AERATION TANK No.	I	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2229	INFLUENT COD(mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD:MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT
Vorticella was found.

TABLE 4S6-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM   (CONTINUOUS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge g Aniline/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
810	0.363	2.42	0.270	0.11
1620	0.727	1.62	0.430	0.27
2430	1.09	1.45	0.323	0.22
8060	3.62	1.78	0.753	0.42
4050	1.82	1.35	1.67	1.24
3240	1.45	1.94	0.808	0.42
6460	2.90	1.24	0.700	0.57

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING

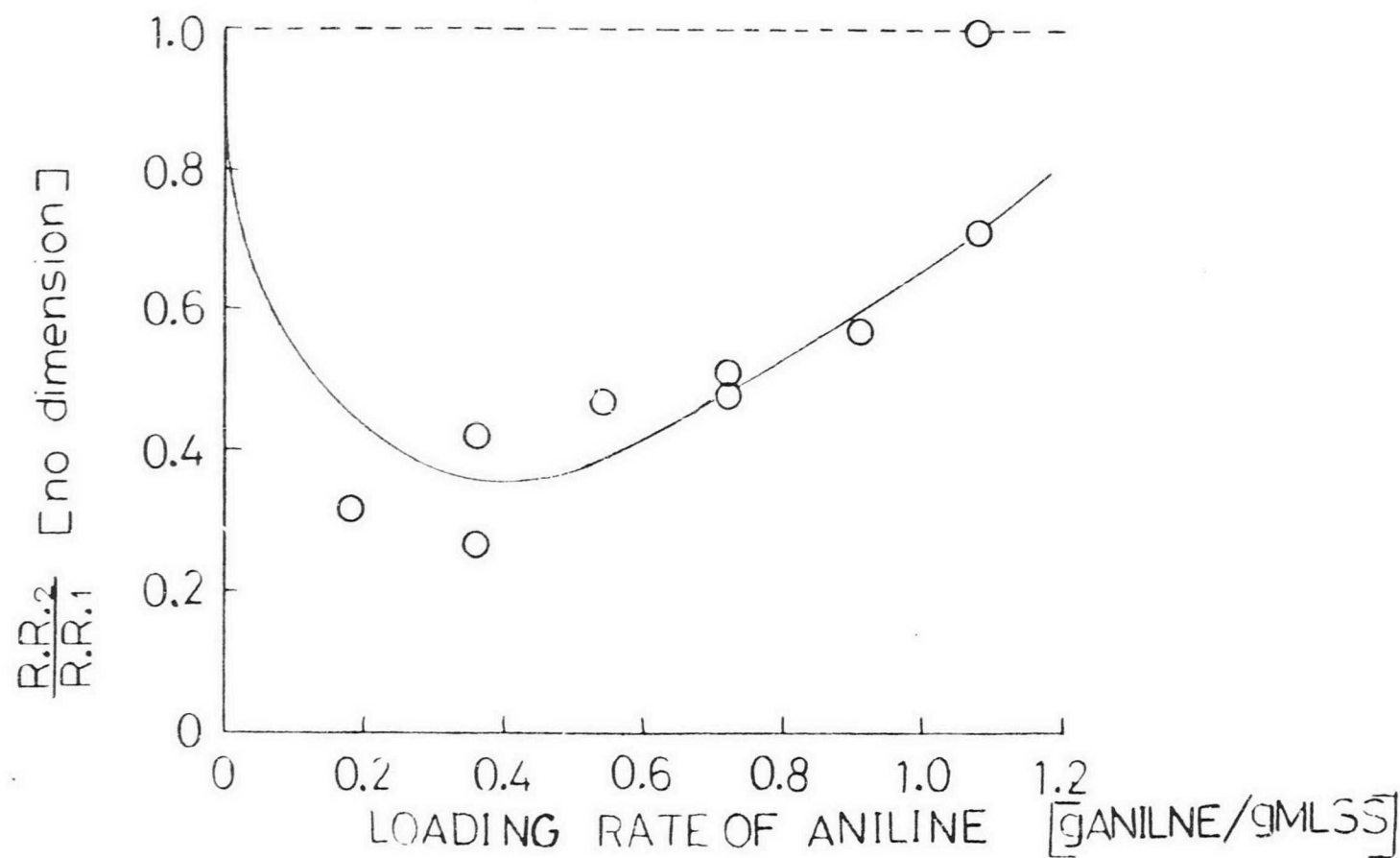$r.r_2$ ------ RESPIRATION RATE AFTER LOADING

Fig. 4S6-1   EFFECT OF ANILINE ON RESPIRATION RATE OF CONTINUOUSLY CULTURED ACTIVATED SLUDGE

4S7-0

DATE 10/25

AERATION TANK No.	I	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2086	INFLUENT COD(mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 4S7-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM ___ (CONTINUOS FEEDING)

Concentration of Aniline ppm	Loading rate with activated sludge g Aniline/gMLSS	$r.r._1$ $\frac{mgO_2}{hr\,gMLSS}$	$r.r._2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.r._1}{r.r._2}$ no dimension
4060	1.95	2.47	1.84	0.74
2040	0.978	1.50	0.633	0.42
1220	0.585	1.21	0.460	0.38
8090	3.88	0.575	0.0575	0.10
6080	2.91	0.575	0.748	1.30
5070	2.43	1.09	1.27	1.16
5680	2.72	0.920	1.61	1.75
6890	3.30	0.978	1.21	1.24
3250	1.56	0.748	0.863	1.15
820	0.393	0.460	0.173	0.38
4470	2.14	1.32	1.27	0.96

$r.r._1$ ······ RESPIRATION RATE BEFORE LOADING

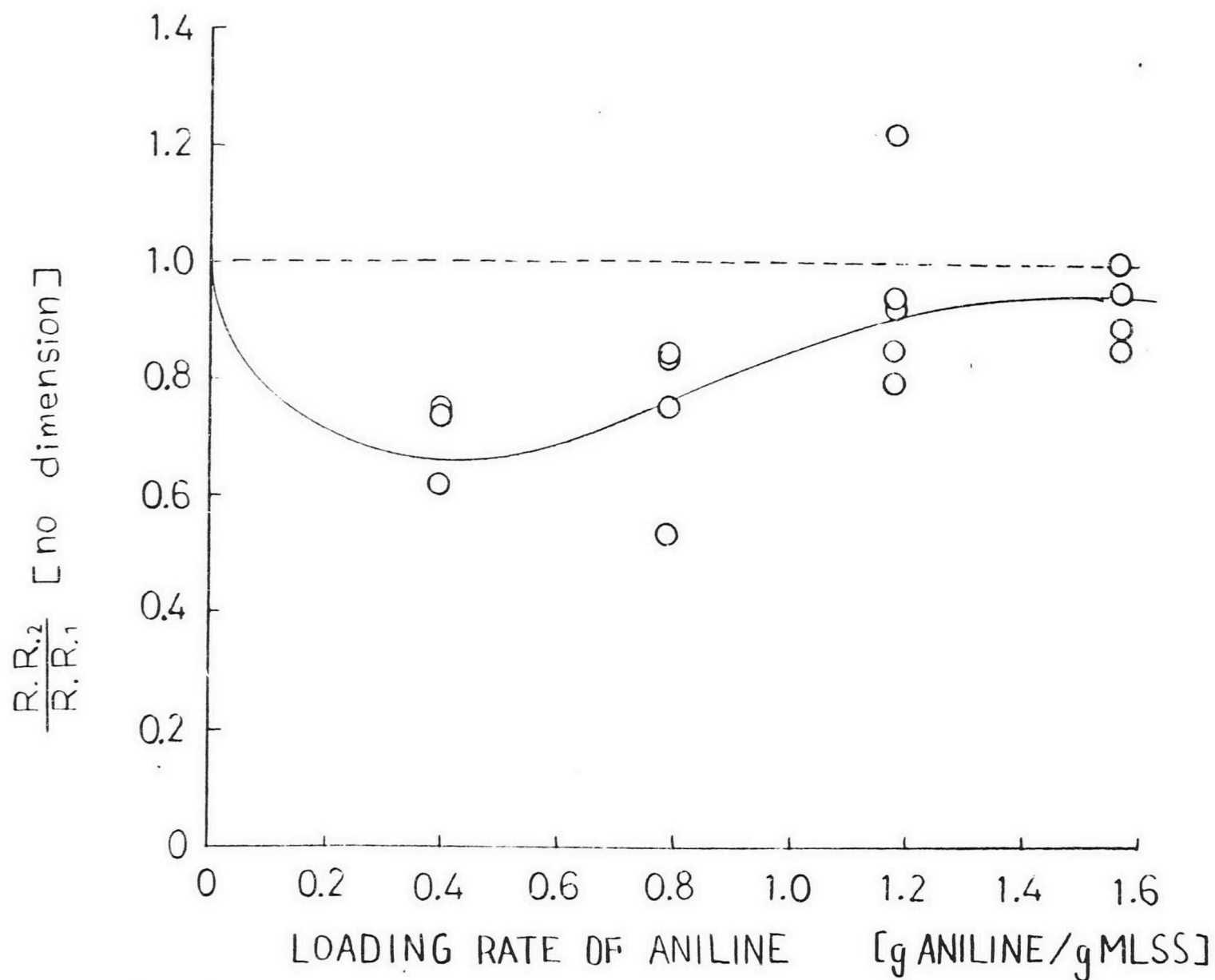$r.r._2$ ······ RESPIRATION RATE AFTER LOADING
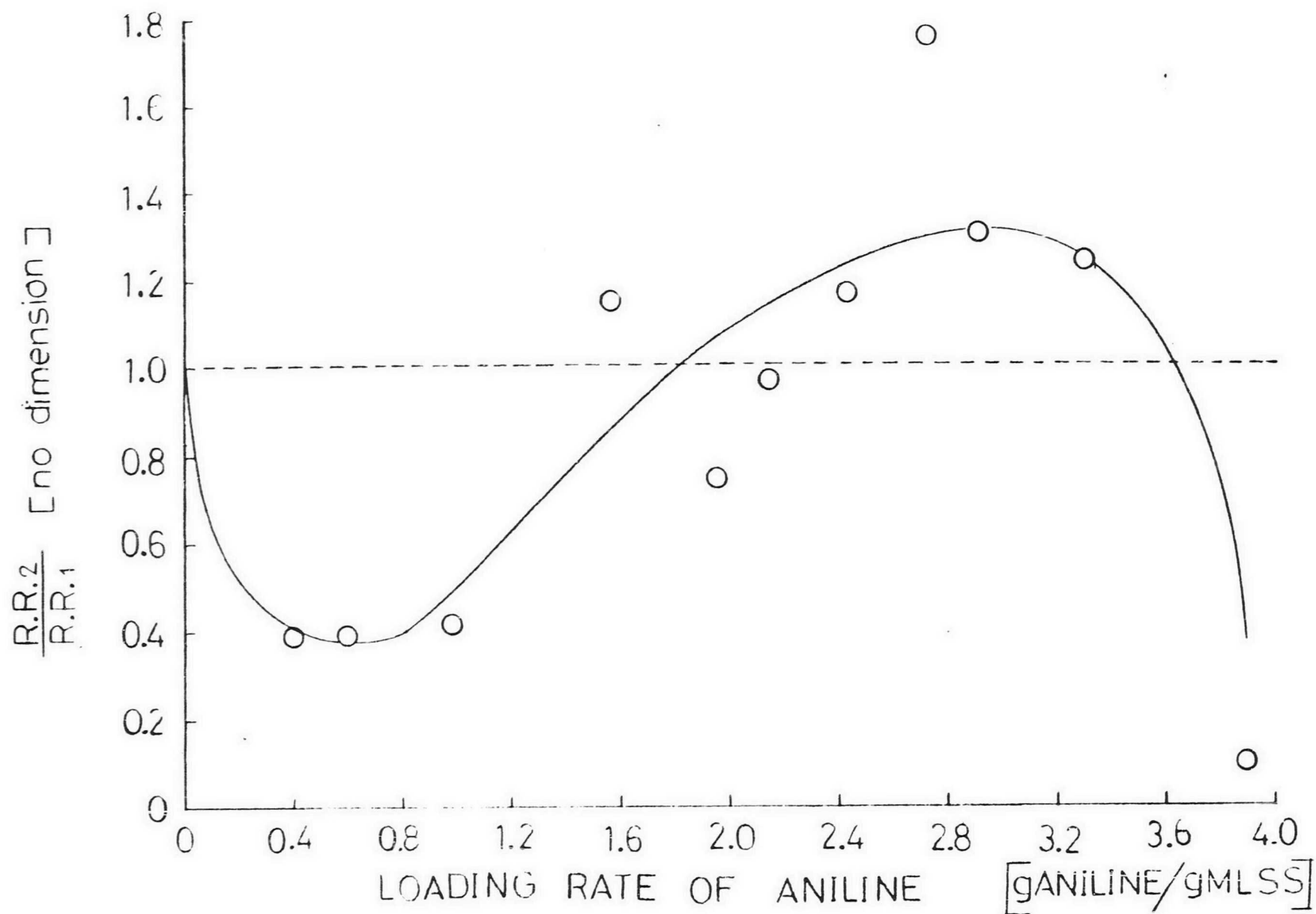
Fig 4 S7-1   EFFECT OF ANILINE ON RESPIRATION RATE OF CONTINUOUSLY CULTURED ACTIVATED SLUDGE

4S8-0

DATE 10/31

AERATION TANK No.	I	LOADING CONDITION	Nitro.n feeding
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON-CENTRATION (mg/l) D O		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1096	INFLUENT COD (mg/l) COD_{in}	——
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	——
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	——
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT
Vorticella was not found.

TABLE 4S8-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM (ENDOTENOUS)

Concentration of Aniline ppm	Loading rate with activated sludge g Aniline/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
4060	3.70	4.15	2.30	0.55
2040	1.86	2.53	1.32	0.52
1020	0.931	2.08	1.32	0.63
200	0.182	0.985	0.548	0.56
100	0.0912	1.75	1.10	0.63
51	0.0465	1.10	1.42	1.30
20	0.0182	0.875	1.21	1.38
10	9.12×10^{-3}	0.548	1.10	2.00
4	3.65×10^{-3}	1.21	1.21	1.00
2	1.82×10^{-3}	0.985	0.985	1.00

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ------ RESPIRATION RATE AFTER LOADING
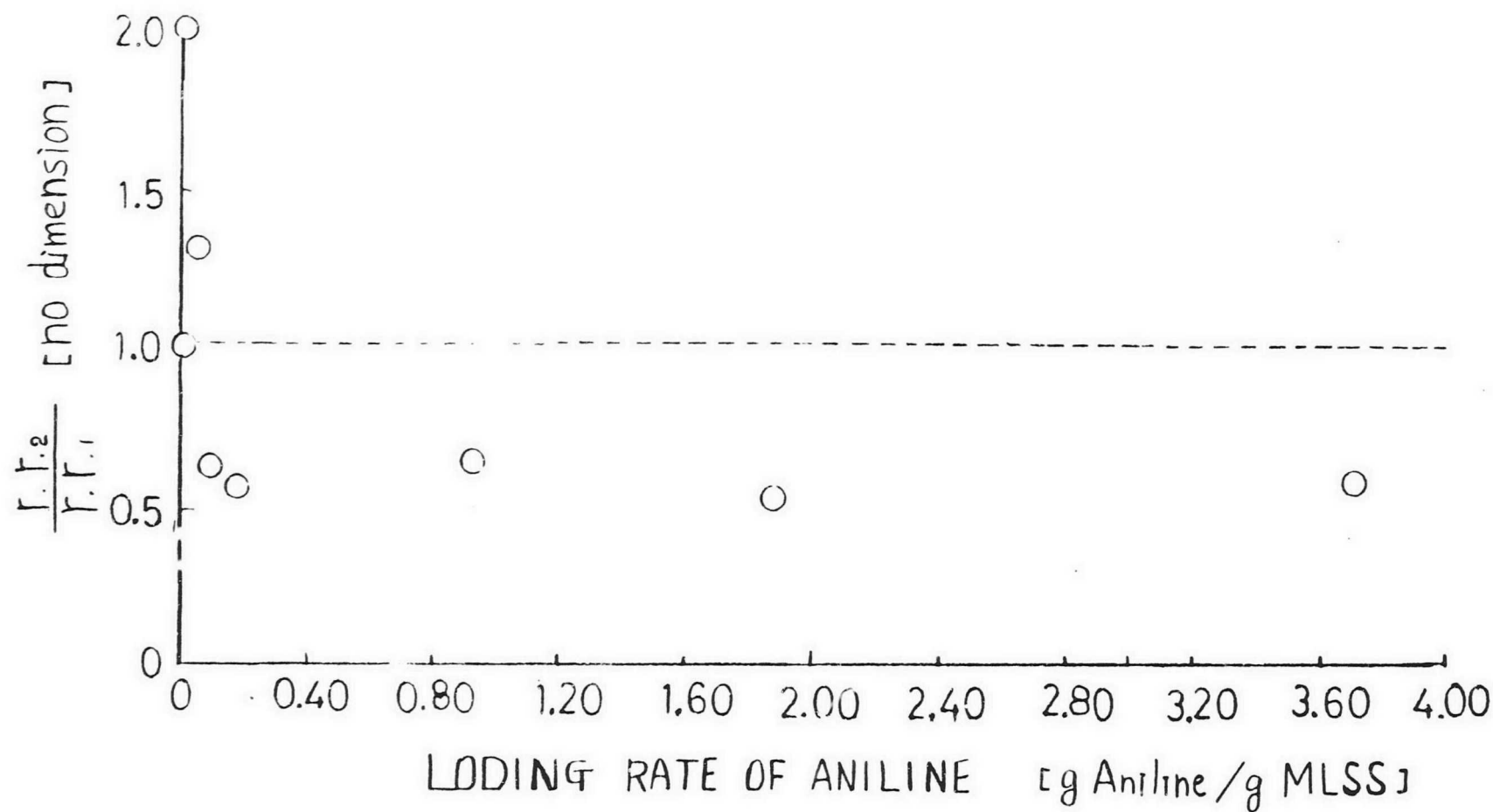
Fig 4S8-1 EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED
SLUDGE SYSTEM (ENDGENOUS)

439-0

DATE 11/3

AERATION TANK No.	I	LOADING CONDITION	Without feeding
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1194	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml/gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l/day)		FOOD : MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/hr·gMLSS)	
MICROSCOPIC OBSERVATION & COMMENT			

Vorticella was not found.

TABLE 459-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM (ENDGENOUS)

Concentration of Aniline ppm	Loading rate with activated sludge gAniline/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
2040	1.71	2.76	1.63	0.59
200	0.168	3.02	1.26	0.42
200	0.168	1.63	1.51	0.92
82	0.0687	1.26.	0.879	0.70
82	0.0687	1.26	1.26	1.00
200	0.168	1.26	1.26	1.00

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING
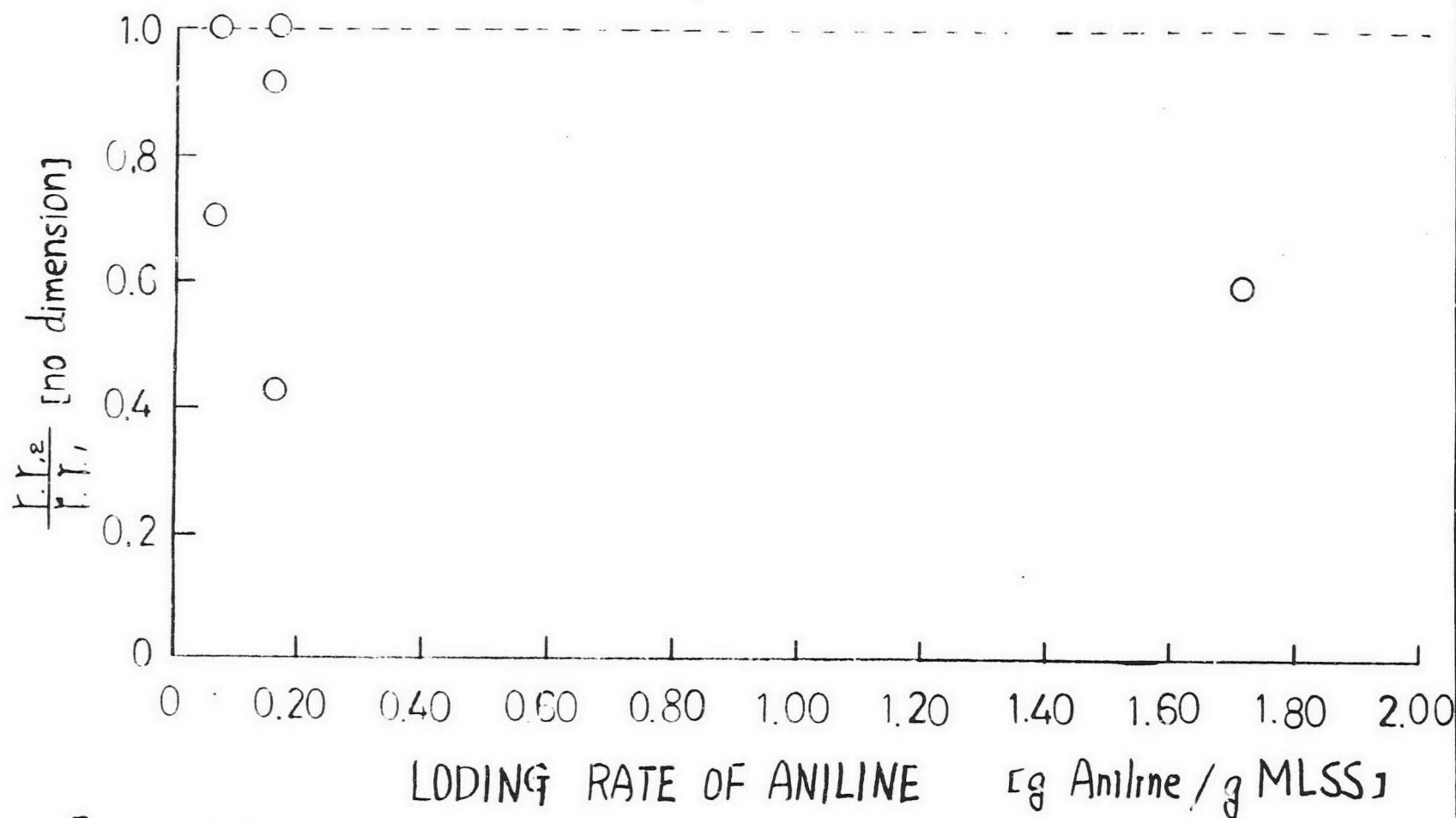
$r.r_2$ ------ RESPIRATION RATE AFTER LOADING

Fig. 4S9-1   EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED
SLUDGE SYSTEM (ENDGENOUS)

DATE 10/27

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	7.45
DISSOLVED OXYGEN CON- CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2162	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	16.5	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	76.3	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was found.

TABLE 4S10-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED
SLUDGE SYSTEM   (BATCH FEEDING)

TIME min	$p^!$	$r.r_1$ $\frac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.r_1}{r.r_2}$ no dimension
0.	7.45	1.87	2.29	1.23
2	7.40	11.2	7.50	0.67
10	7.37	4.48	4.18	0.93
19	7.38	2.50	3.62	1.45
30	7.40	2.00	3.07	1.53
45	7.42	2.50	3.67	1.48
60	7.47	1.68	2.18	1.30
79	7.50	1.55	2.43	1.56
100	7.56	2.05	2.51	1.21
130	7.60	1.80	2.11	1.17
160	7.61	1.50	2.36	1.58
210	7.67	1.31	2.68	2.

$r.r_1$ ------ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ------ RESPIRATION RATE AFTER LOADING

Fig. 4S10-1   pH CHANGE AFTER ADITION
OF CSL

Fig 4S10-2 CHANGE OF R.R1 AFTER ADDITION
OF CSL

Fig 4S10-3   CHANGE OF R.R. RATIO AFTER ADDITION OF CSL
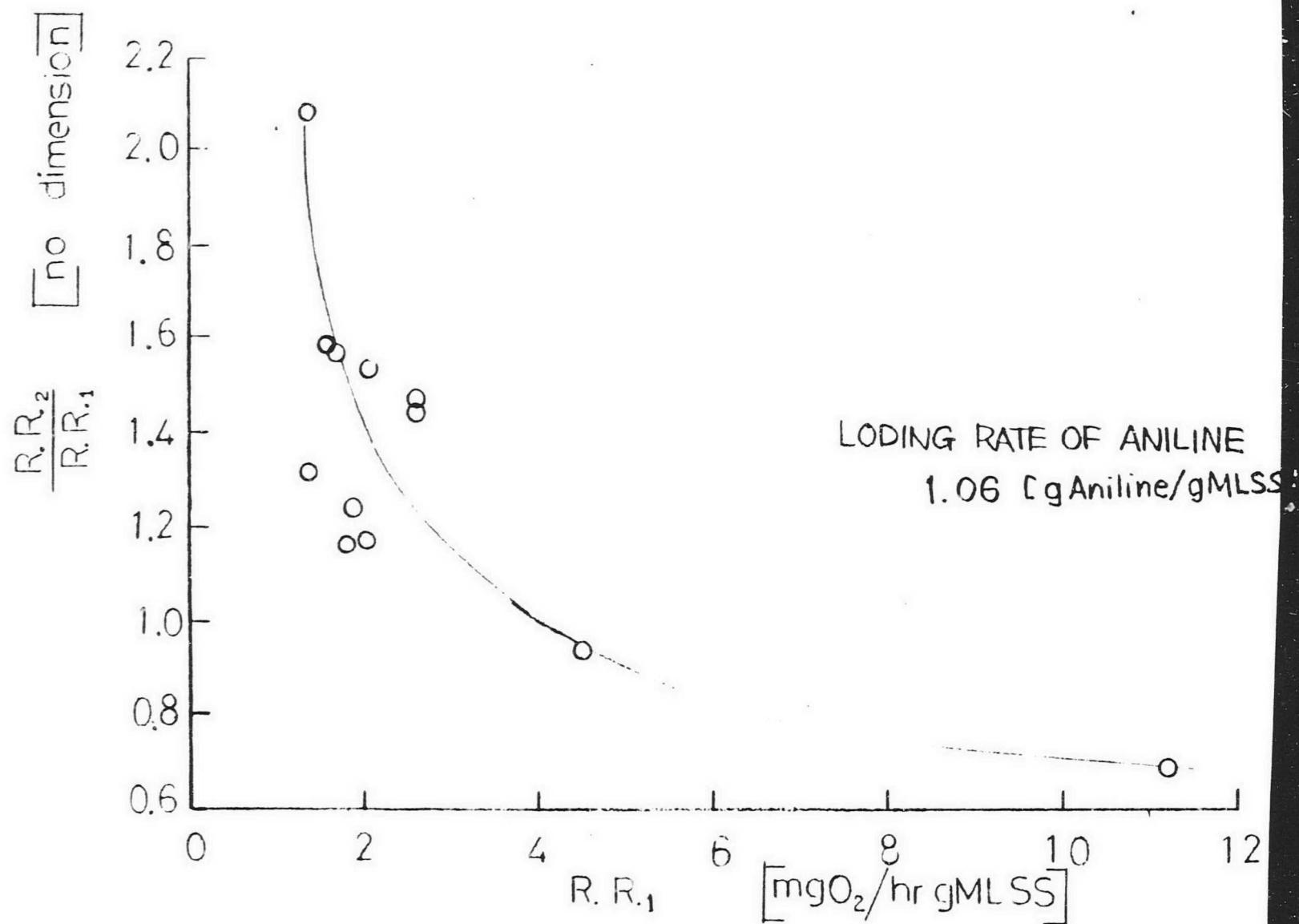
Fig 4S10-4. DIFFERENCE IN RESPIRATION RATE RATIO WITH RESPIRATI RATE OF ACTIVATED SLUDGE SOLUTION

4S11 - 0

DATE 11/1

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON- CENTRATION (mg/l) D O		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1022	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l/day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was not found.

TABLE 4511-0

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM   (BATCH   FEEDING)

TIME min	pH	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
0-		4.67	2.62	0.56
1		12.3	5.60	0.45
8		4.11	1.76	0.43
20		1.77	0.587	0.33
40		1.47	1.47	1.00

$r.r_1$ ...... RESPIRATION RATE BEFORE LOADING

$r.r_2$ ...... RESPIRATION RATE AFTER LOADING

Fig. 4S11-2   CHANGE OF R.R.₁
            AFTER ADDITION
            OF CSL

Fig. 4S11-3 CHANGE OF R.R. RATIO
AFTER ADDITION OF
CSL
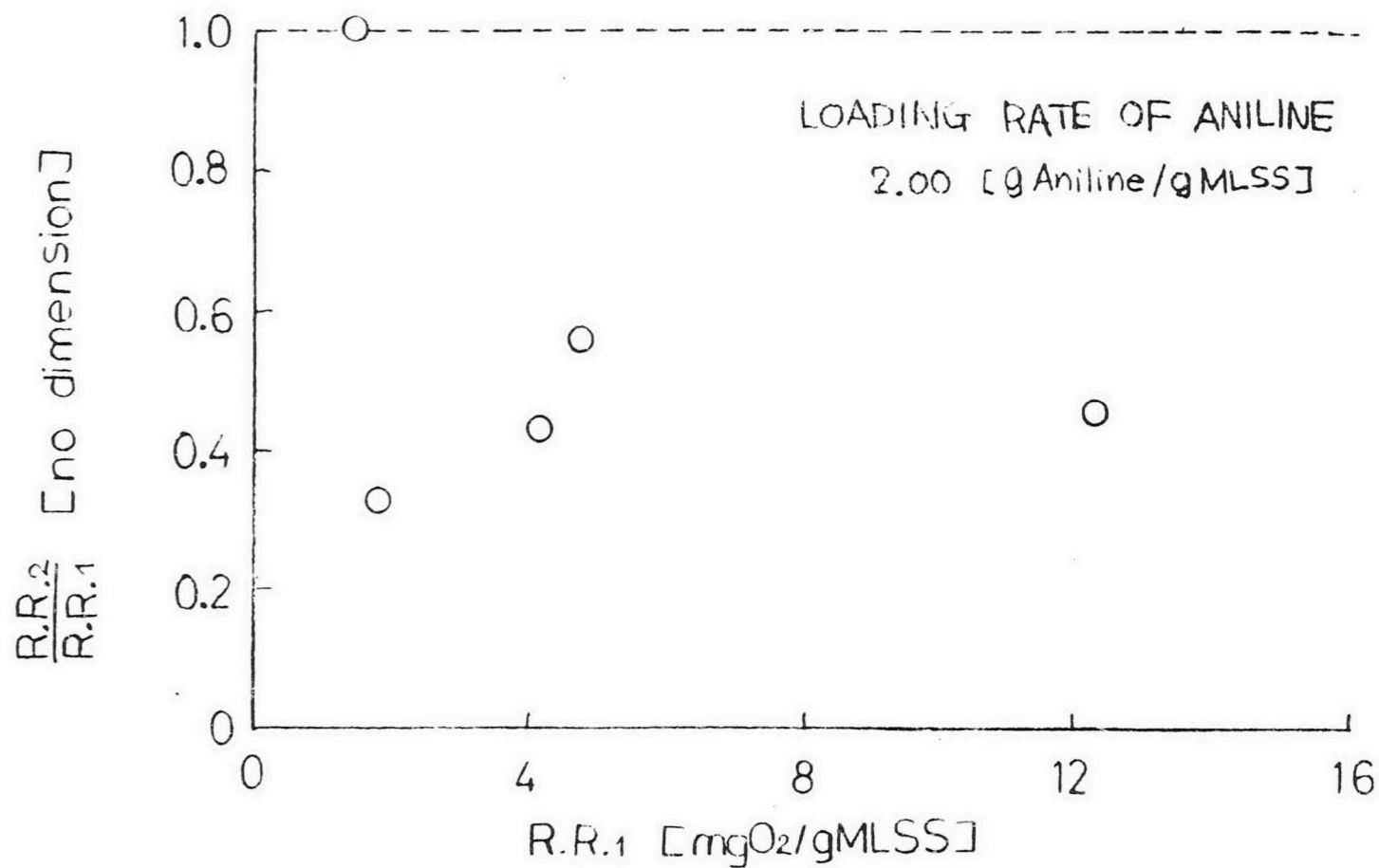
Fig.4SII-4 DIFFERENCE IN RESPIRATION RATE RATIO
WITH RESPIRATION RATE OF ACTIVATED
SLUDGE SOLUTION

4S12 - 0

DATE 11/7

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	
DISSOLVED OXYGEN CON- CENTRATION (mg/l) D O		OXIDATION – REDUCTION POTENTIAL (mV) O R P	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	644	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	3.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	46.6	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was not found.

TABLE 4.S12-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM (BATCH FEEDING)

TIME min	pH	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$ no dimension
0.	7.29			
2	7.29	20.7	14.4	0.70
12	6.78	21.0	17.5	0.83
15	6.38			
20	6.20	17.9	12.1	0.68
34	6.13	21.0	11.4	0.54
60	6.42	17.9	10.9	0.61
88	6.62	13.5	9.32	0.69
113	6.72	13.5	3.49	0.26
154	6.80	9.32	3.03	0.33
198	6.84	3.96	3.03	0.76
225	6.88	2.10	0.699	0.33
246	6.88	5.82	1.86	0.32

$r.r_1$ ⸱⸱⸱⸱⸱⸱ RESPIRATION RATE BEFORE LOADING

$r.r_2$ ⸱⸱⸱⸱⸱⸱ RESPIRATION RATE AFTER LOADING
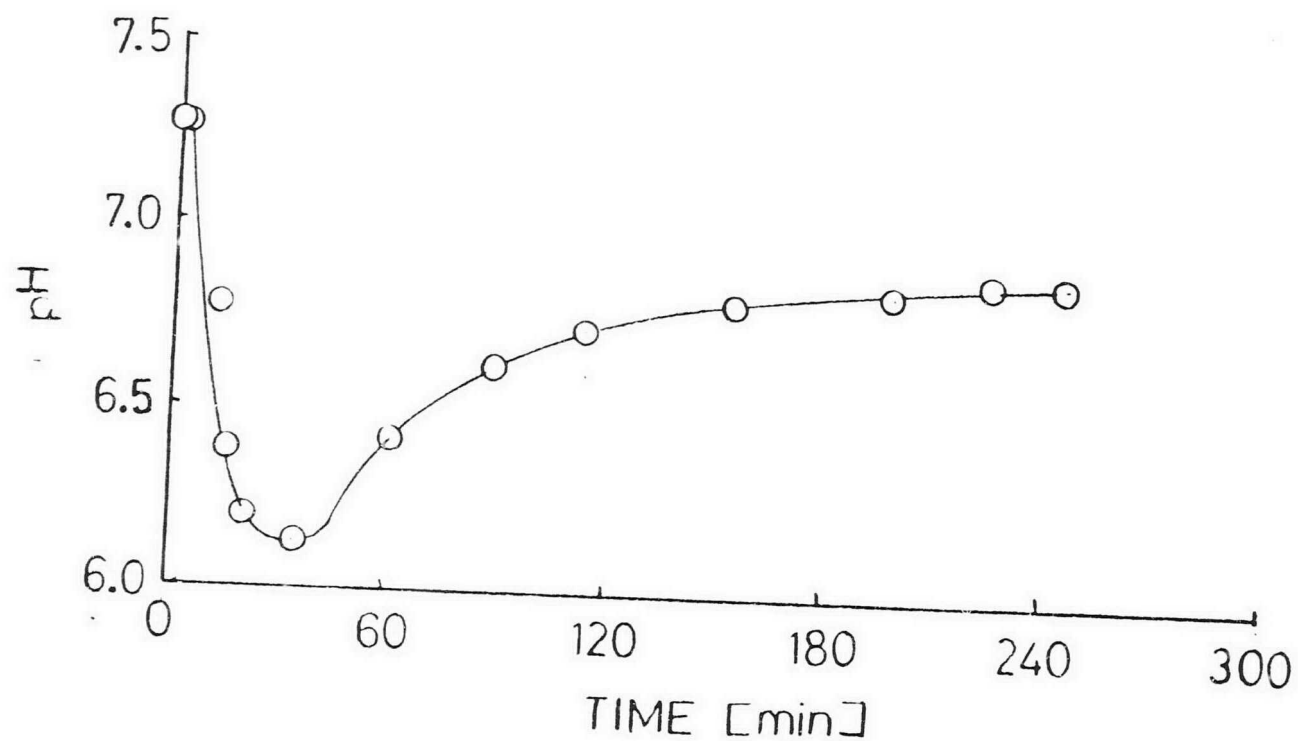
Fig 4S. 12-1   pH CHANGE AFTER ADDITION OF CSL
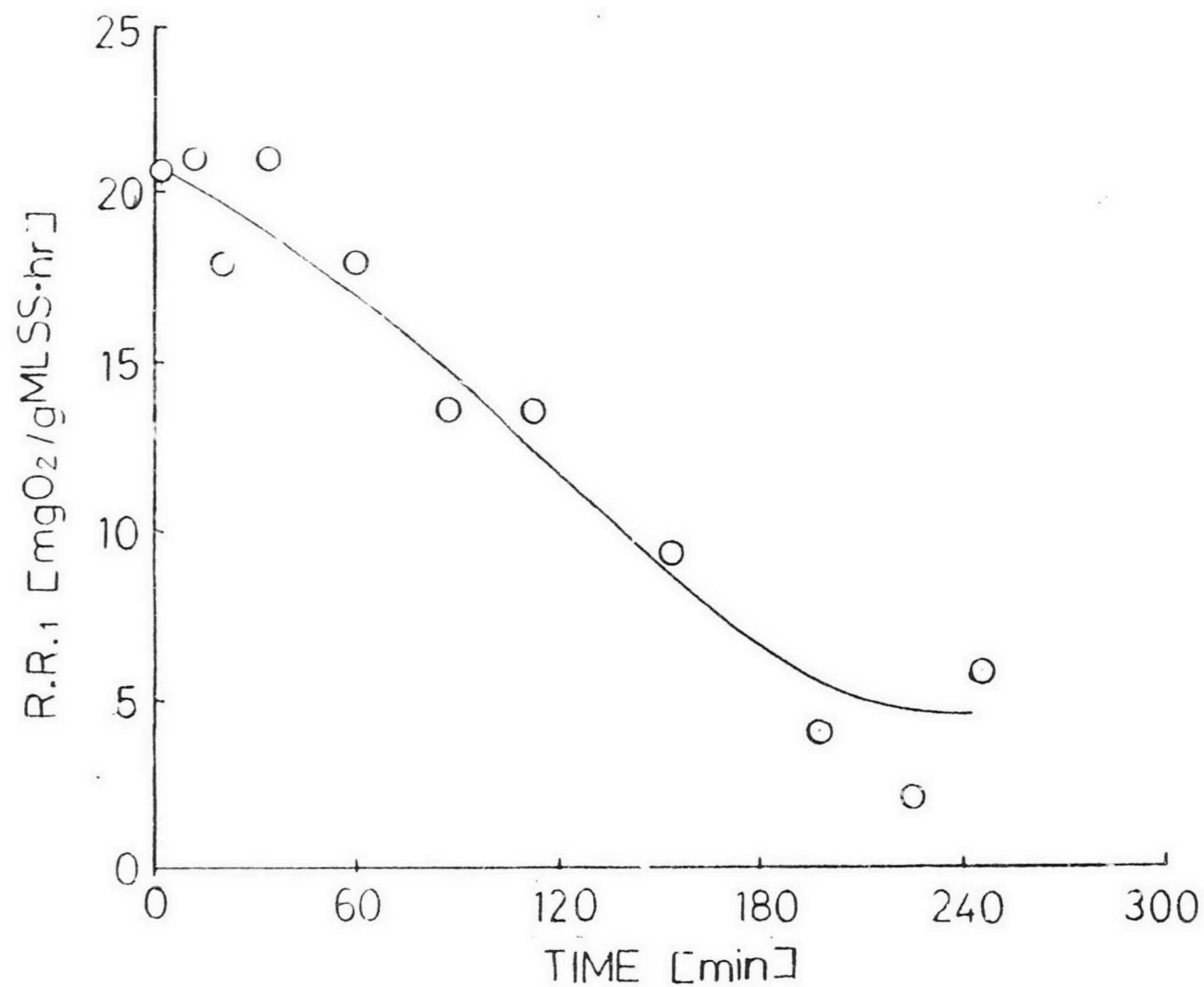
Fig. 4S12-2 CHANGE OF R.R.1 AFTER ADDITION OF CSL
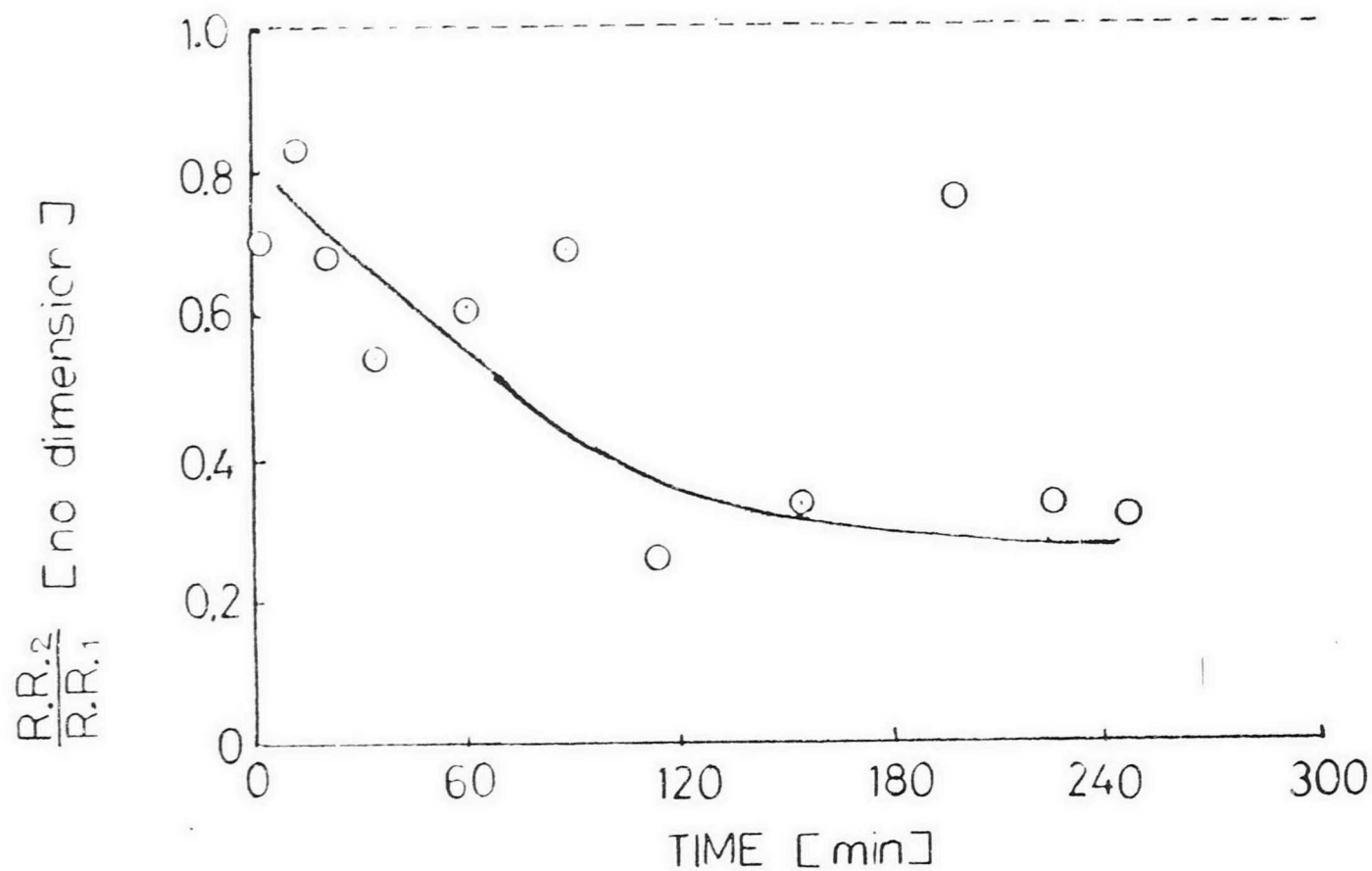
Fig 4S12-3 CHANGE OF R.R. RATIO AFTER ADDITION OF CSL
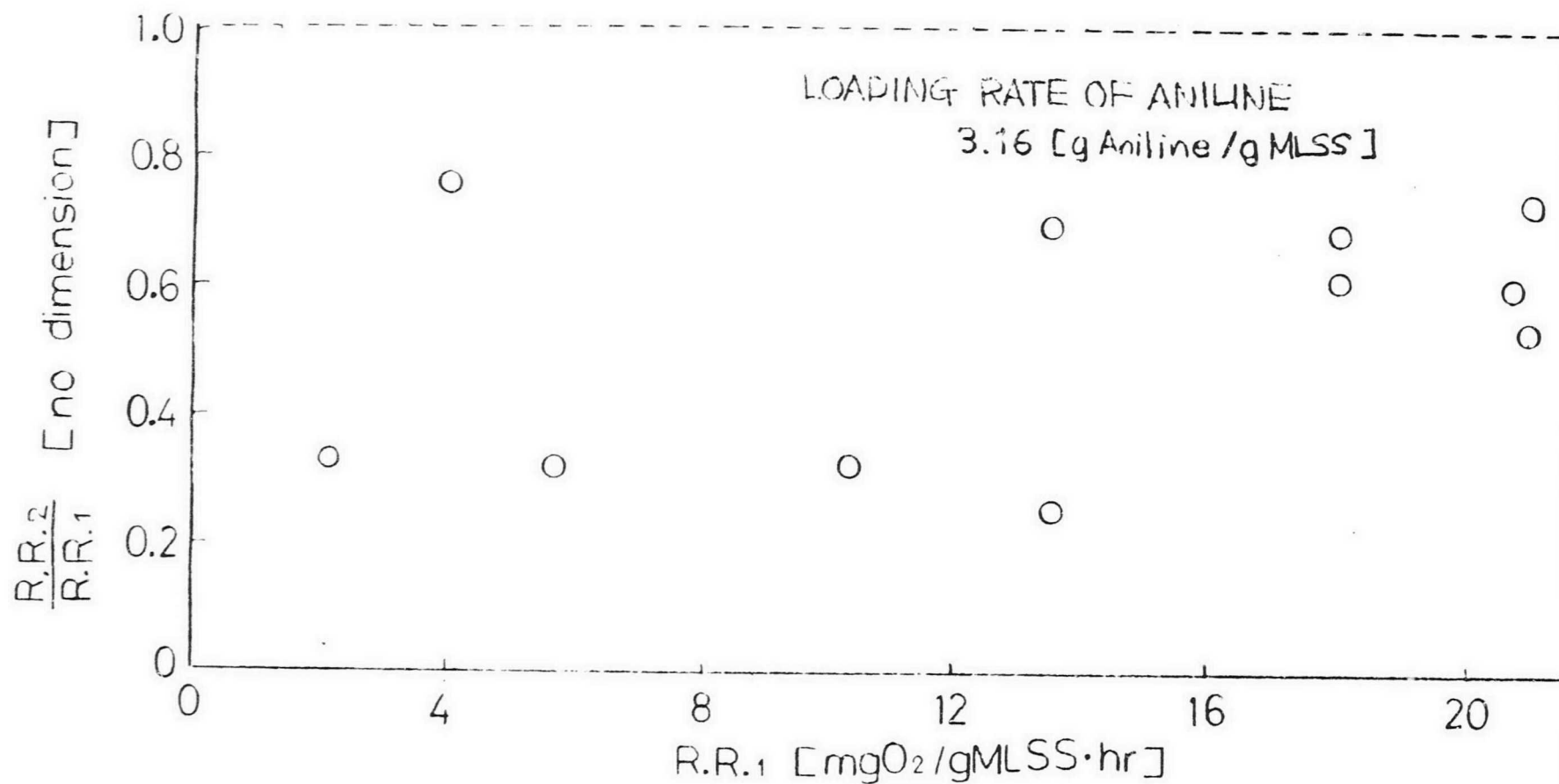
Fig 4S12-4   DIFFERENCE IN RESPIRATION RATE RATIO
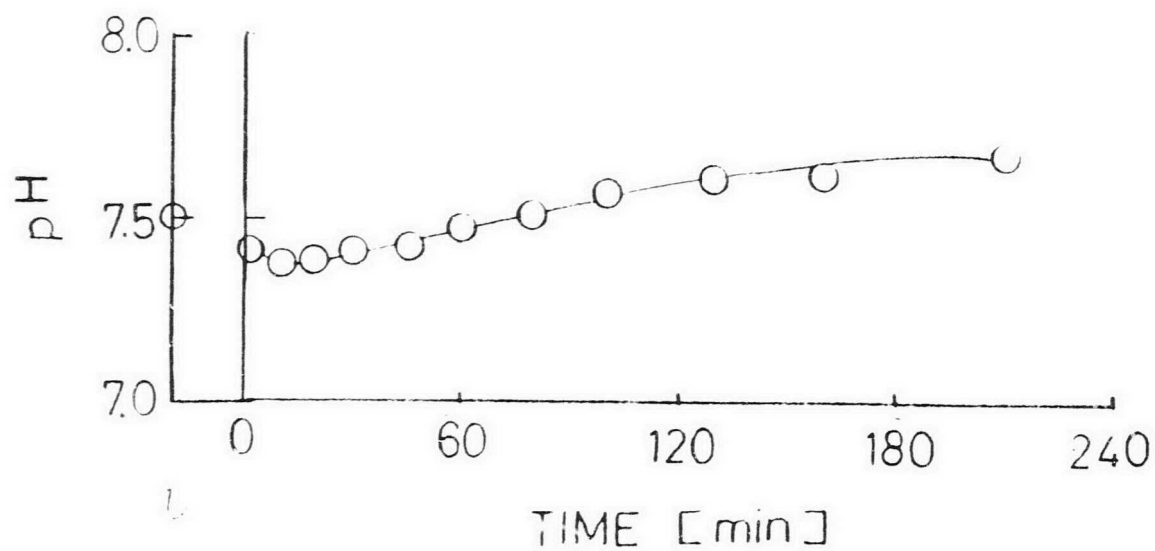WITH RESPIRATION RATE OF ACTIVATED
SLUDGE SOLUTION

4513-0

DATE 11/5

AERATION TANK No.	V	LOADING CONDITION	Excess loading
TEMPERATURE (°C) T		pH	4.51
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	3416	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)	——	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})	——	RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella and Rotifera vere not found.

TABLE 4SI3-1

EFFECT OF ANILINE ON RESPIRATION RATE OF ACTIVATED SLUDGE SYSTEM   (BATCH FEEDING)

TIME min	pH	r. r.$_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	r. r.$_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.\,r._1}{r.\,r._2}$ no dimension
0 -				
2	4.51	18.4	16.2	0.88
11	4.75	18.4	15.8	0.86
21	5.01	15.3	14.1	0.92
32	5.30			
42	5.49	14.4	13.5	0.94
52	5.91	13.5	12.3	0.91
69	6.00			
82	6.11	11.6	9.48	0.82
96	6.20	11.2	8.08	0.73
114	6.30	7.90	6.14	0.78
131	6.30	6.32	4.22	0.68

r. r.$_1$ ------ RESPIRATION RATE BEFORE LOADING

r. r.$_2$ ------ RESPIRATION RATE AFTER LOADING
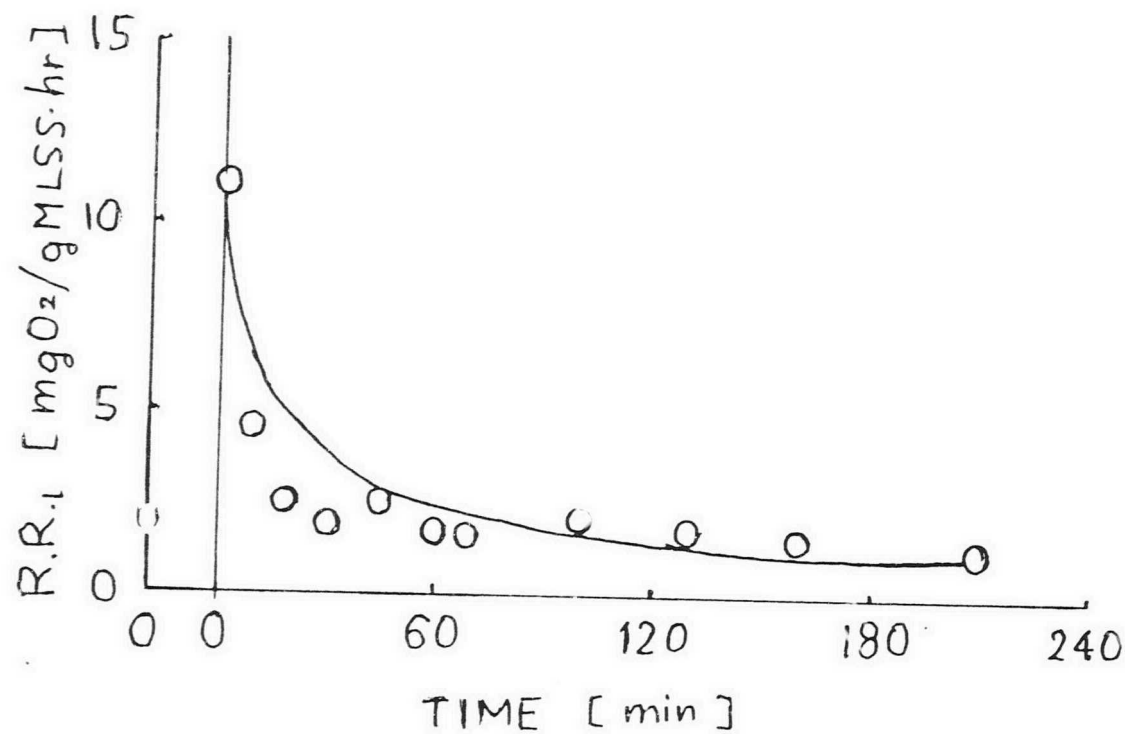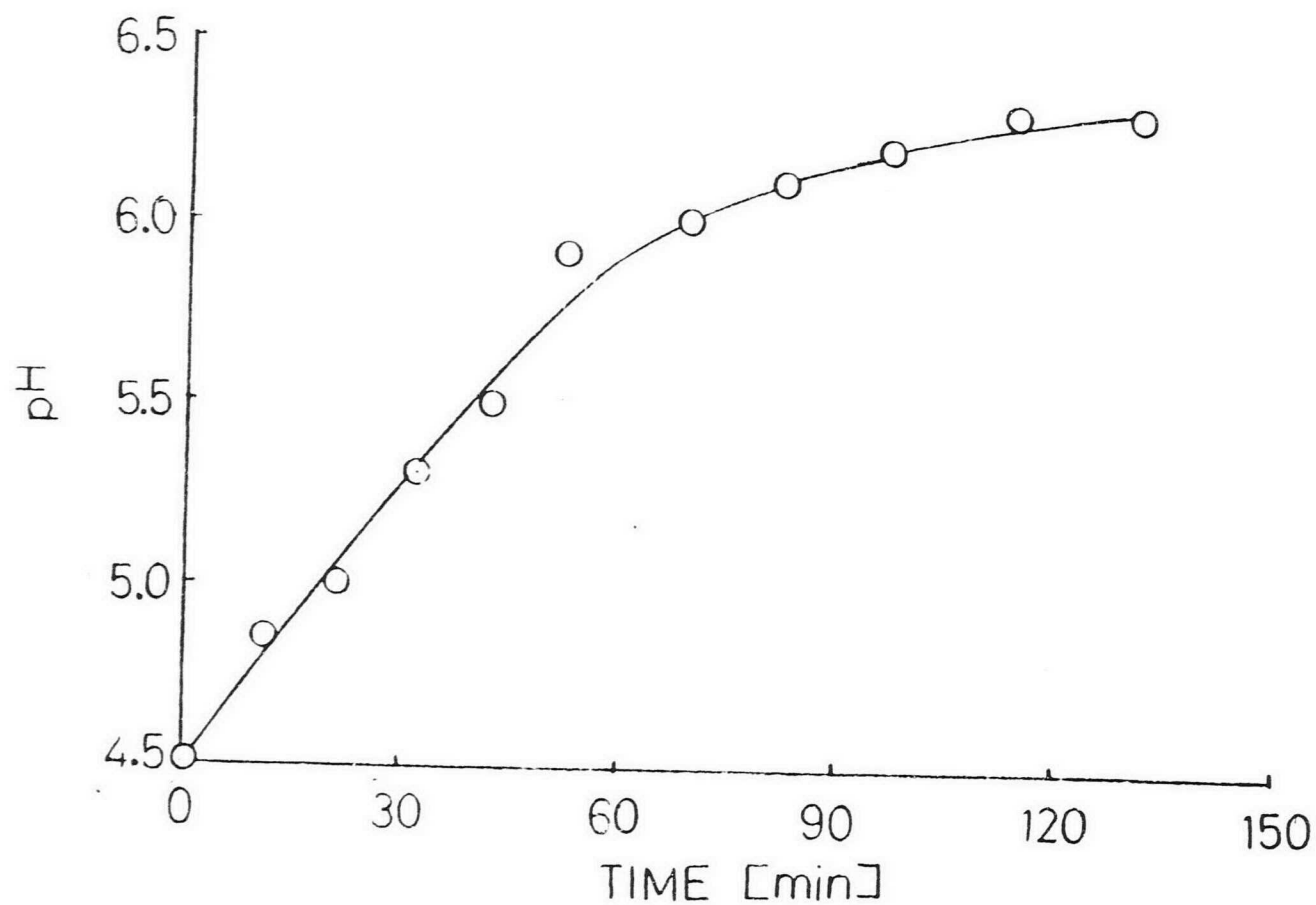
Fig. 4S13-1   pH CHANGE AFTER ADDITION OF CSL
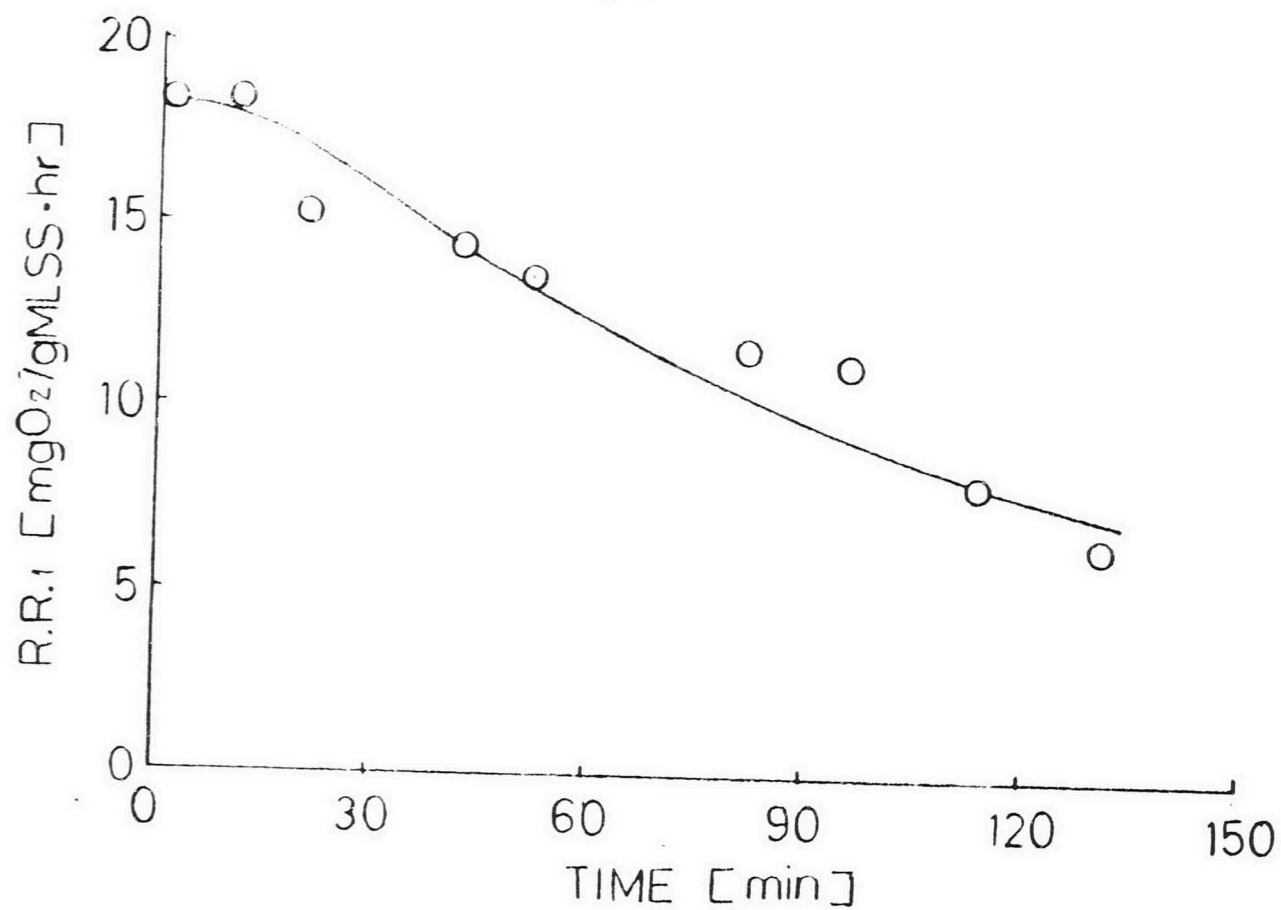
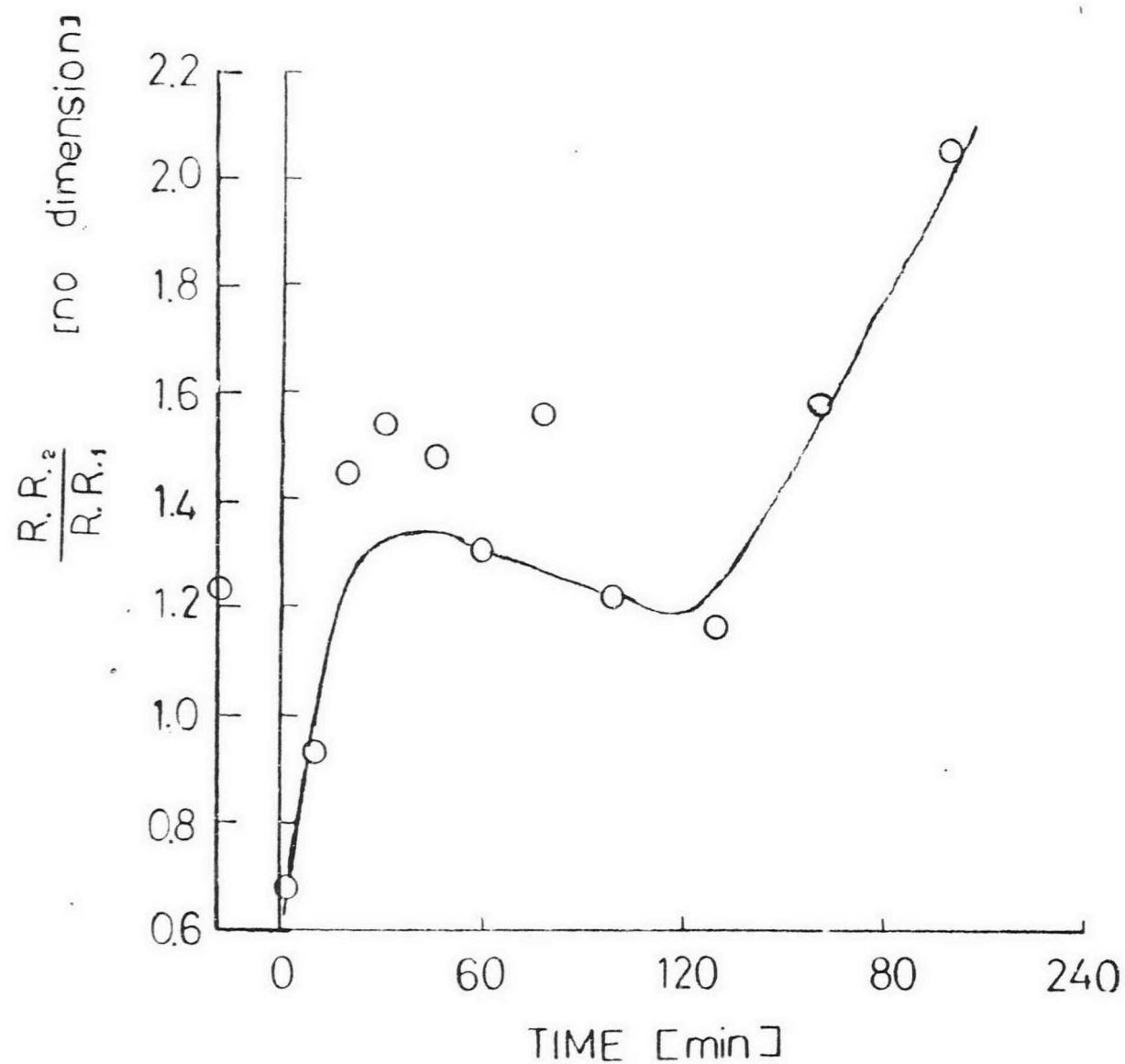Fig. 4S13-2. CHANGE OF R.R.1 AFTER ADDITION
OF CSL
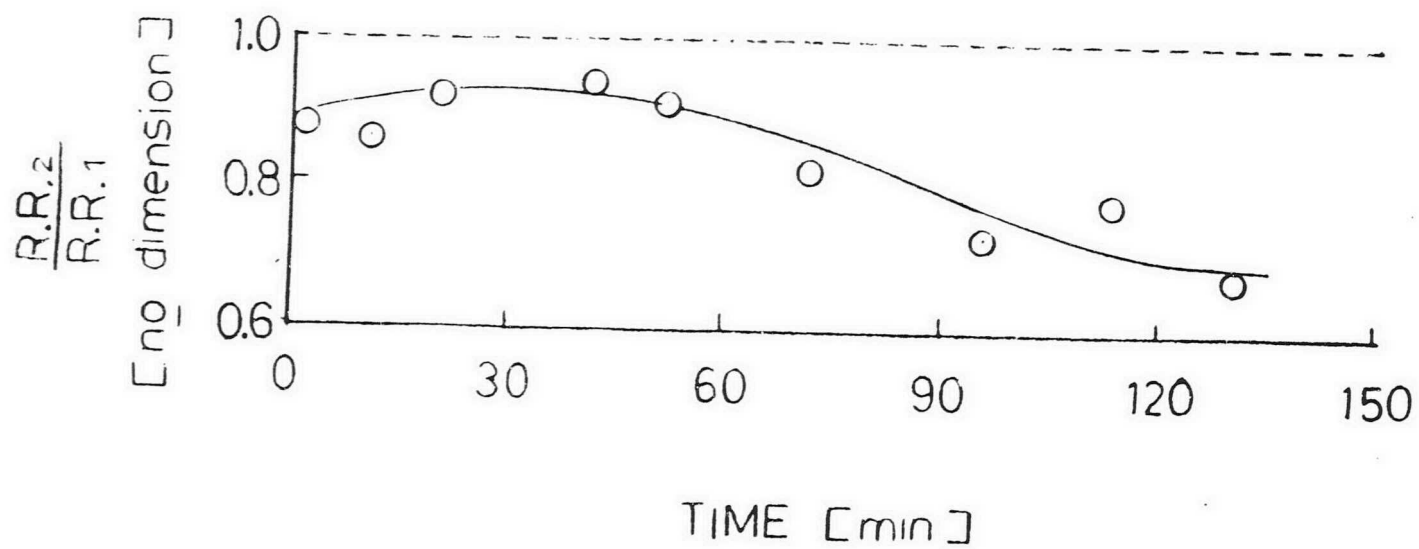
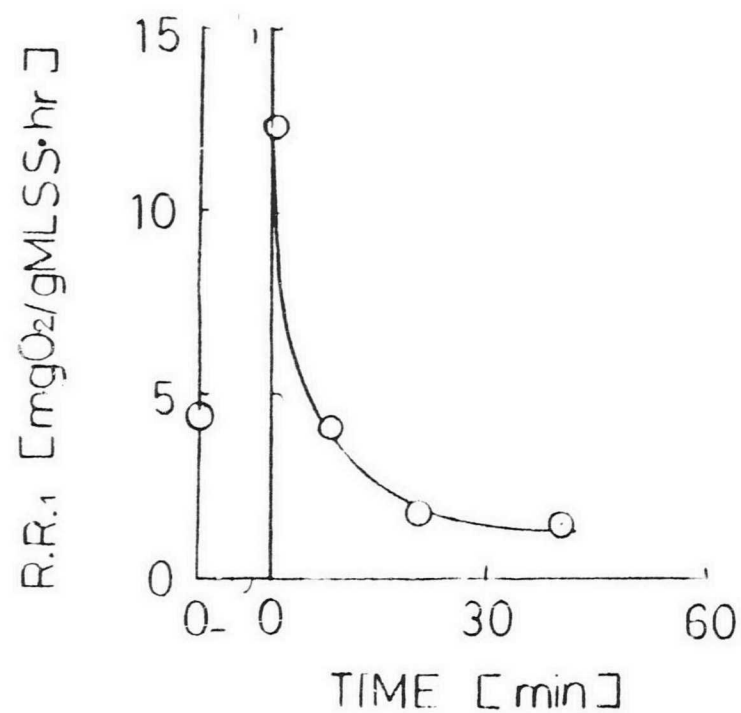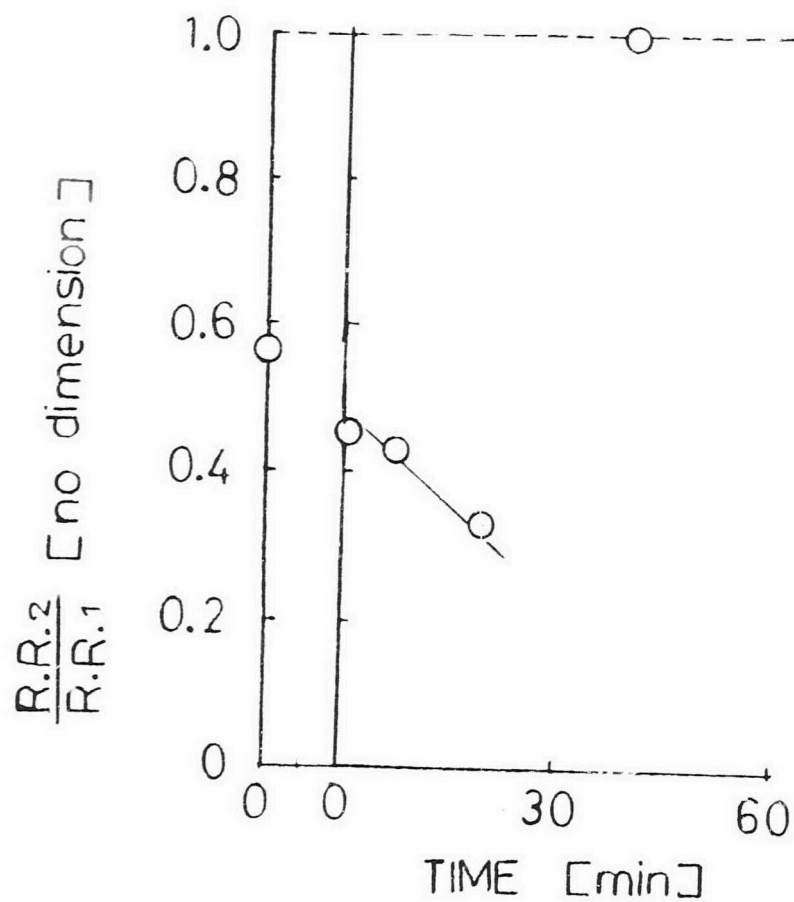Fig. 4513-3. CHANGE OF R.R. RATIO AFTER ADDITION
OF CSL
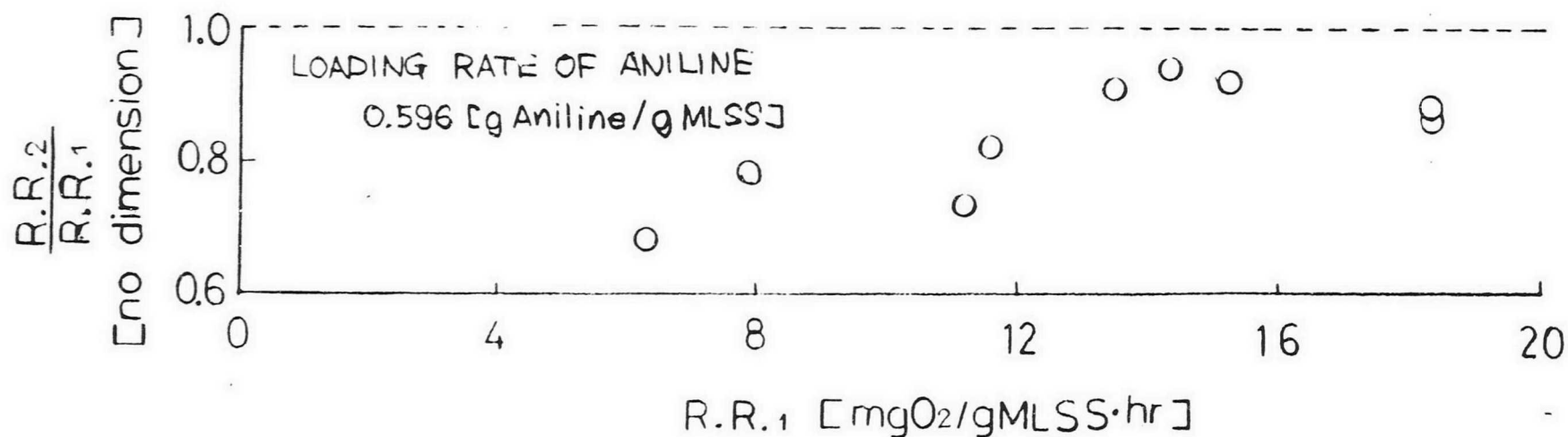
Fig 4S13-4. DIFFERENCE IN RESPIRATION RATE RATIO
WITH RESPRATION RATE OF ACTIVATED
SLUDGE SOLUTION

5. The Effect of Waste Water Containing Hydrolyzed Tolylene
    diisocyanate on Activated Sludge

5.1 Introduction

Tolylene diisocyanate (TDI) is fairly reactive with water
to produce variety of amines and polyureas as described
in the preceding chapter. Thus, the vapor of tolylene
diisocyanate can be absorbed with water. The waste water may
include the various reaction products along with unreacted
TDI,which may become a cause of secondary pollution.
The waste water which has absorbed TDI might be introduced
into the biological waste water treatment plant.
Thus, in this chapter the effect of reaction products
which came from the hydrolysis of TDI on the activated
sludge was investigated.
The effect was evaluated by measuring the respiration
rates of activated sludge before and after the addition
of sample solution in the same manner as Chapter 4.
The theoretical base of this evaluation was that the waste
water treatment by activated sludge was the aerombic
reaction. In other words, the main reaction was the
consumption of oxygen. Thus, the rate of consuming oxygen
would be a measure of the activity of the biological
system.

5.2   Experimental

The sample solution for the examination was prepared as
follows.

Tolylene diisocyanate of 2 vol. % was well mixed with
water and was kept at room temperature for some period.
White suspended matter was formed through the reaction
and was precipitated.   The solution with suspension was
stored to complete the hydrolysis of TDI.   The solution
thus prepared was well stirred and then used as a sample.
The preparation of activated sludge and the measurement
of the respiration rate were exactly same as those in
Chapter 4.   They should be referred if necessary.
In this chapter, the apparent concentration of TDI was
used i.e. the concentration of TDI meant the quotient of
the weight of TDI added by the weight of a material under
consideration and the hydrolysis reaction was left out of
account.

5.3   Results

5.3.0   The number of tables and figures

In this chapter, a few experimental data are shown as a
set exactly same as in Chapter 4.
Accordingly, the special numbering way was employed.
The independent tables and figures were numbered in the
same way as preceding chapters.

A set of tables and figures were given in the following principle.

```
5 SY - X
│ │     │_____ Number of chapter
│ │_____ Set number of experiment
│_____ Number of table and figure in
                             the set of experiment
```
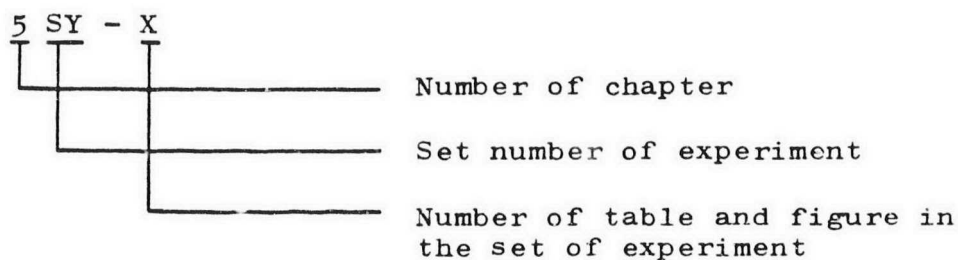
Tables for $X = 0$ such as 5S5-0, 5S8-0, offer the data on the activated sludge used for the set of experiments. The data for tank I was not included in this report. The precise data on the culture can be obtained in Chapter 2 in this report if needed.

5.3.1 <u>Effect of hydrolyzed TDI on the activated sludges</u>
      <u>cultured under various conditions</u>

The respiration rate of the activated sludge obtained under continuous culture changed when hydrolyzed TDI was given as shown in Figures 5SY-1 $(X = 1 - 7)$. The x-axis means the apparent loading rate, i.e., the quotient of added TDI (g) by MLSS (g) though the solution containing the products of hydrolyzed TDI was given actually.

As seen in these figures $r.r._2/r.r._1$ was almost proportional to the apparent loading rate.

When the slope was positive, the hydrolyzed TDI solution
seemed to be a substrate and vice versa.

The hydrolyzed TDI could be both substrate and inhibitor
depending on the conditions of culture.

Figure 5S8-1 shows the change in respiration rate of the
activated sludge cultured without feeding CSL.

In this case, the respiration rate slightly changed with
addition of hydrolyzed TDI.

5.3.2 The effect of the time of TDI hydrolysis

The changes in the respiration rate of the same activated
sludges for the solutions of different hydrolysis time
are given in Figures 5S6-1 and 5S6-2.

The solution immediately after the mixing of TDI and water
inhibited the respiration, while after two days aging the
solution accelerated the respiration.

However, this tendency was not always obvious for the
different activated sludge as shown in Fig. 5S7-1.

Thus, the more precise experiment would be needed to
clarify the effect of hydrolysis.

5.3.3 The relation of r.r.2/r.r.1 with r.r.1 for the activated sludge whose state changed continuously

The activated sludge was aerated without the substrate
for a day or more

until the respiration rate became low enough. After the respiration mode attained endogenous condition, the corn steep liquor was added.

The change in pH and respiration rate with time after the addition of corn steep liquor are given in Figures 5SX-1 and 5SX-2 (X = 9, 10, and 11), respectively.

When the loading rate of hydrolyzed TDI was as low as 0.0440 (g/g MLSS) $r.r._2/r.r._1$ was a slightly larger than unity as seen in Figure 5S9-3 and it was not affected by $r.r._1$ (Figure 5S9-4).

In the case of loading rate 0.661 (g/g MLSS), the value of $r.r._2/r.r._1$ was between 0.9 and 1.1 (Figure 5S10-3). $r.r._2/r.r._1$ was related with $r.r._1$ as shown in Figure 5S10-4.

When the loading of hydrolyzed TDI was so high as 1.45 (g/g MLSS), $r.r._2/r.r._1$ stayed at 0.3 to 0.6 (Figure 5S11-3). The corelation between $r.r._2/r.r._1$ and $r.r._1$ was not found (Figure 5S11-4).

The experiments of 5S9-X, 5S10-X, and 5S11-X showed that

(1) the very diluted solution of hydrolyzed TDI did not give the effect on the activated sludge system.

(2) the solution of high concentration inhibited the activity of the activated sludge.

5.3.4 Response of over loaded activated sludge to the addition of hydrolyzed TDI

was The activated sludge cultured under a relatively high loading condition.

The response of the respiration rate to the addition of hydrolyzed TDI is plotted in Figure 5S13-1. The plot in this figure was obtained from the two different activated sludges shown in Tables 5S12-0 and 5S13-0.

This plot indicated that the respiration activity was accelerated for the low loading of hydrolyzed TDI and vice versa.

5.4 Discussions

1) As appearing in 5SY-1 (Y = 1 to 7), $r.r._2/r.r._1$ was proportional to the loading rate of TDI (= added TDI/MLSS) for the activated sludge of continuous culture. Thus, the proportionality constant, i.e. the slope of line would be an index of the effect given by hydrolyzed TDI.

Corelations of the slope with MLSS, pH, and respiration rate of the activated sludge used were not found. Also, the slope was independent of the biological phase. However, the slope was found to be closely related to SVI and COD of effluent of the activated sludge used.

This slope (S) was given as

$$S = \left(\frac{r.r._2}{r.r._1}\right) / \left(\frac{\text{added TDI (g)}}{\text{MLSS(g)}}\right)$$

The relation of S with SVI and COD of effluent is presented in Table 5.1.

The plots of S against SVI and COD of effluent appear in Figures 5.1 and 5.2, respectively.

These relations indicate that activated sludge system maintaining the low SVI and low COD of effluent is favourable to the treatment of hydrolyzed TDI.

2) The hydrolysis time of TDI did not seem to give the definite difference in the response of activated sludge. It was surmised that TDI reacted with water very rapidly and the composition of products did not change much. This estimation was consistent with that obtained in the preceding chapter.

3) The activated sludge under endogenous conditions was not reactive to the hydrolyzed TDI, while the over-loaded activated sludge was reactive. As long as the loading of TDI was not intense, over-loaded activated sludge could treat hydrolyzed TDI.

5.5 Conclusion

1) $r.r._2/r.r._1$ was found to be proportional to the loading

rate of TDI for the activated sludge of con̲ ̲nuous
culture.

2) The proportionality constant (S) of the above relation
was found to be the functions of SVI and also COD of
effluent. S increased as SVI and COD of effluent
became smaller.

3) The hydrolysis reaction of TDI was estimated to proceed
fairly fast.

4) The activated sludge under endogenous conditions was
not sensitive to the hydrolyzed TDI, while that under
over-loaded conditions responded to it.

5) The value of slope S could be negative or positive
depending upon the condition of activated sludge.
Thus, the biological treatment of the waste water
containing the products of hydrolyzed TDI would be
possible if the appropriate activated sludge was used.
The acclimation of activated sludge with hydrolyzed
TDI could also be expected.

5.6 Useful Informations and Suggestions

1) Judging from the results of 5SY-X (Y = 1 to 7), the
diluted waste water containing hydrolyzed TDI would
give slight effect on the activated sludge system under
the usual conditions.

2) SVI and COD of effluent would be important parameters
   to control the activated sludge plant which treat the
   waste water containing hydrolyzed TDI.

5 S1 - 0

DATE 11/14

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE ($^\circ$C) T	23.0	pH	4.32
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO	0.8	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2218	INFLUENT COD (mg/l) COD_{in}	41.5
SPECIFIC VOLUME SV_{30}	10.8	EFFLUENT COD (mg/l) COD_{eff}	13.2
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	48.7	REMOVAL EFFICIENCY OF COD (%)	63.2
INFLUENT WATER FLOW RATE (l/day)	236	FOOD : MICROORGANISM RATIO F/M (gCOD / gMLSS·day)	0.043
HYDRAULIC DETENTION TIME (hr^{-1})	10.0	RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 5 : 1
Vorticella and Rotifera were not active
Effluent was not clear and not viscous.

TABLE
5S1-1
RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSly CULTURED ACTIVATED SLUDGE)

ADDED TDI SLUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gMLSS	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	$\dfrac{r.\ r._2}{r.\ r._1}$
97	0.0437	10.7	11.6	1.09
49	0.0221	9.75	10.3	1.05
150	0.0676	10.3	11.4	1.11
240	0.108	10.3	11.6	1.13
490	0.221	9.75	12.5	1.28
340	0.153	9.75	11.8	1.21
24	0.0108	10.2	11.2	1.11
190	0.0857	10.3	11.6	1.13

r. r.$_1$ ------ RESPIRATION RATE BEFORE LOADING

r. r.$_2$ ------ RESPIRATION RATE AFTER LOADING

Fig. 5SH. RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

5S2-0

DATE 11/15

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE ($^\circ$C) T	23.0	pH	6.62
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.65	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2335	INFLUENT COD (mg/l) COD_{in}	65.8
SPECIFIC VOLUME SV_{30}	13.5	EFFLUENT COD (mg/l) COD_{eff}	14.0
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	57.8	REMOVAL EFFICIENCY OF COD (%)	73.6
INFLUENT WATER FLOW RATE (l/day)	207	FOOD:MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	0.059
HYDRAULIC DETENTION TIME (hr^{-1})	11.3	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 2:1
Vorticella was active.

Effluent was not clear and not viscous.

TABLE 5S2-1   RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSly CULTURED ACTIVATED SLUDGE)

ADDED TDI	ADDED TDI	r. r.$_1$	r. r.$_2$	$\dfrac{r.\ r._2}{r.\ r._1}$
SLUTION WEIGHT	MLSS			
ppm	g TDI/gMLSS	mgO$_2$/hr gMLSS	mgO$_2$/hr gMLSS	
49	0.0210	11.3	14.8	1.31
97	0.0415	10.0	12.8	1.28
240	0.103	11.6	15.2	1.31

r. r.$_1$ ······ RESPIRATION RATE BEFORE LOADING

r. r.$_2$ ······ RESPIRATION RATE AFTER LOADING

Fig. 5S2-1. RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

5S3-0

DATE 11/18

AERATION TANK　No.	I/	LOADING CONDITION	Contin-uous
TEMPERATURE　(°C)　T	24.0	pH	5.30
DISSOLVED OXYGEN CON-CENTRATION　(mg/l)　DO	1.2	OXIDATION – REDUCTION POTENTIAL　(mV)　ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l)　MLSS	2636	INFLUENT COD(mg/l)　COD_{in}	93.2
SPECIFIC VOLUME　SV_{30}	23.0	EFFLUENT COD　(mg/l)　COD_{eff}	27.3
SLUDGE VOLUME INDEX (ml/gMLSS)　SVI	106	REMOVAL EFFICIENCY OF COD　(%)	70.7
INFLUENT WATER FLOW RATE　(l/day)	236	FOOD：MICROORGANISM RATIO　F/M (gCOD/gMLSS·day)	0.085
HYDRAULIC DETENTION TIME　(hr⁻¹)	10.0	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Effluent was not clear with yellow color.

TABLE 5S3-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

ADDED TDI SUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gMLSS	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	$\dfrac{r.\ r._2}{r.\ r._1}$
490	0.186	10.5	9.56	0.91
240	0.0910	9.33	9.33	1.00
390	0.148	9.33	9.10	0.98
150	0.0569	9.56	9.79	1.02
290	0.110	9.10	9.56	1.05
97	0.0368	8.88	9.79	1.10

r. r.$_1$ ...... RESPIRATION RATE BEFORE LOADING

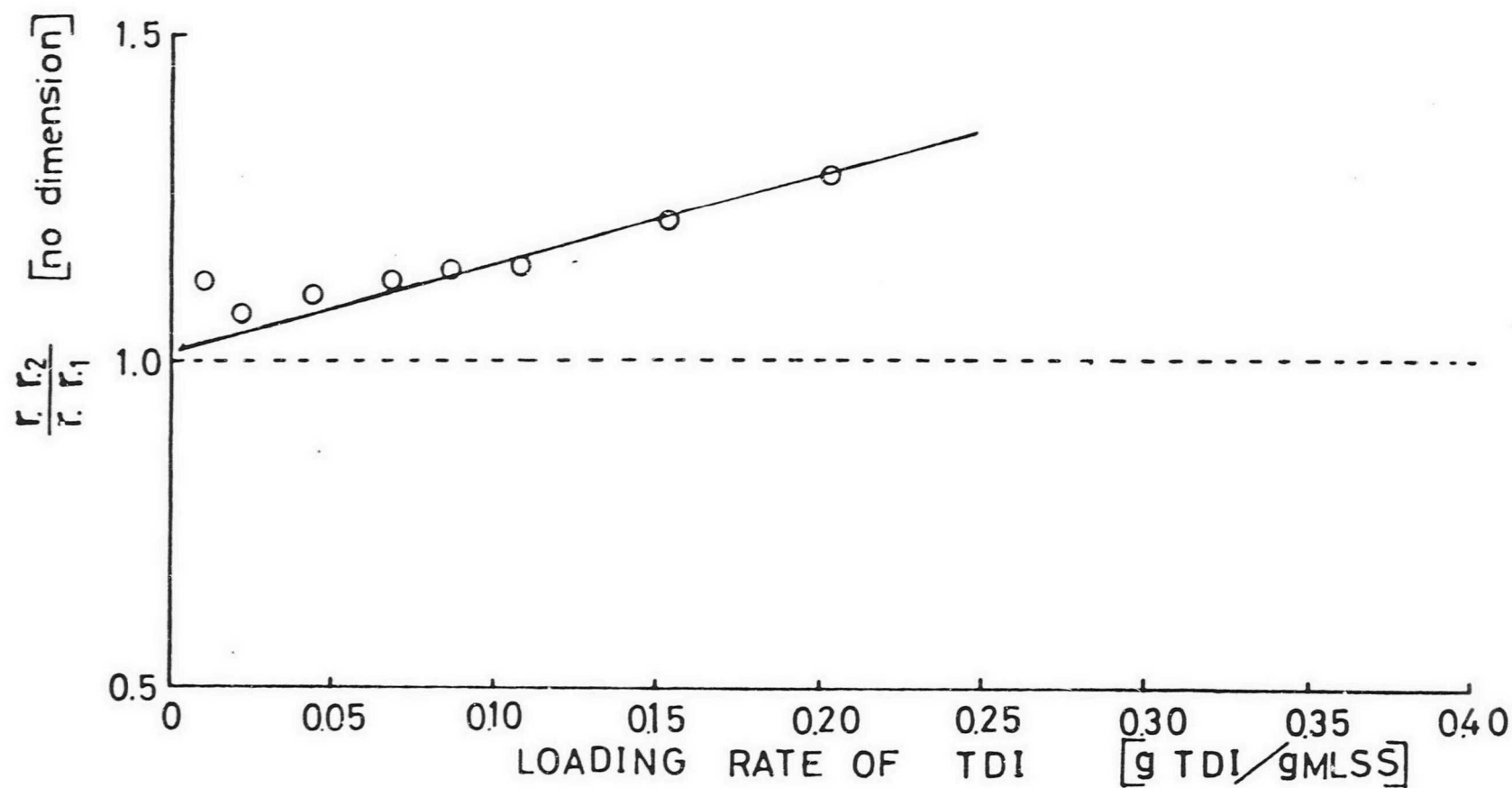r. r.$_2$ ...... RESPIRATION RATE AFTER LOADING

Fig. 5S3-1. RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

5S4-0

DATE 11/20

AERATION TANK No.	1V	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	23.0	pH	5.30
DISSOLVED OXYGEN CON-CENTRATION (mg/l) D O	1.5	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2574	INFLUENT COD(mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	25.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	97.1	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l/day)		FOOD : MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 4 : 4

Vorticella and Rotifera were not active.

Flock was dispersive.

TABLE 5S4.-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

ADDED TDI SLUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gMLSS	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	r. r.$_2$ / r. r.$_1$
490	0.190	11.9	11.2	0.94
240	0.0932	10.5	10.0	0.95
97	0.0377	11.6	11.6	1.00
390	0.152	12.1	11.2	0.92
150	0.0583	12.8	12.1	0.95
290	0.113	12.8	12.3	0.96
190	0.0738	14.4	13.5	0.94
340	0.132	14.0	13.5	0.97
49	0.0190	14.7	14.4	0.98
73	0.0284	16.3	16.3	1.00
49	0.0190	16.8	16.1	0.96
24	9.32×10^{-3}	16.5	16.3	0.99

r. r.$_1$ ...... RESPIRATION RATE BEFORE LOADING

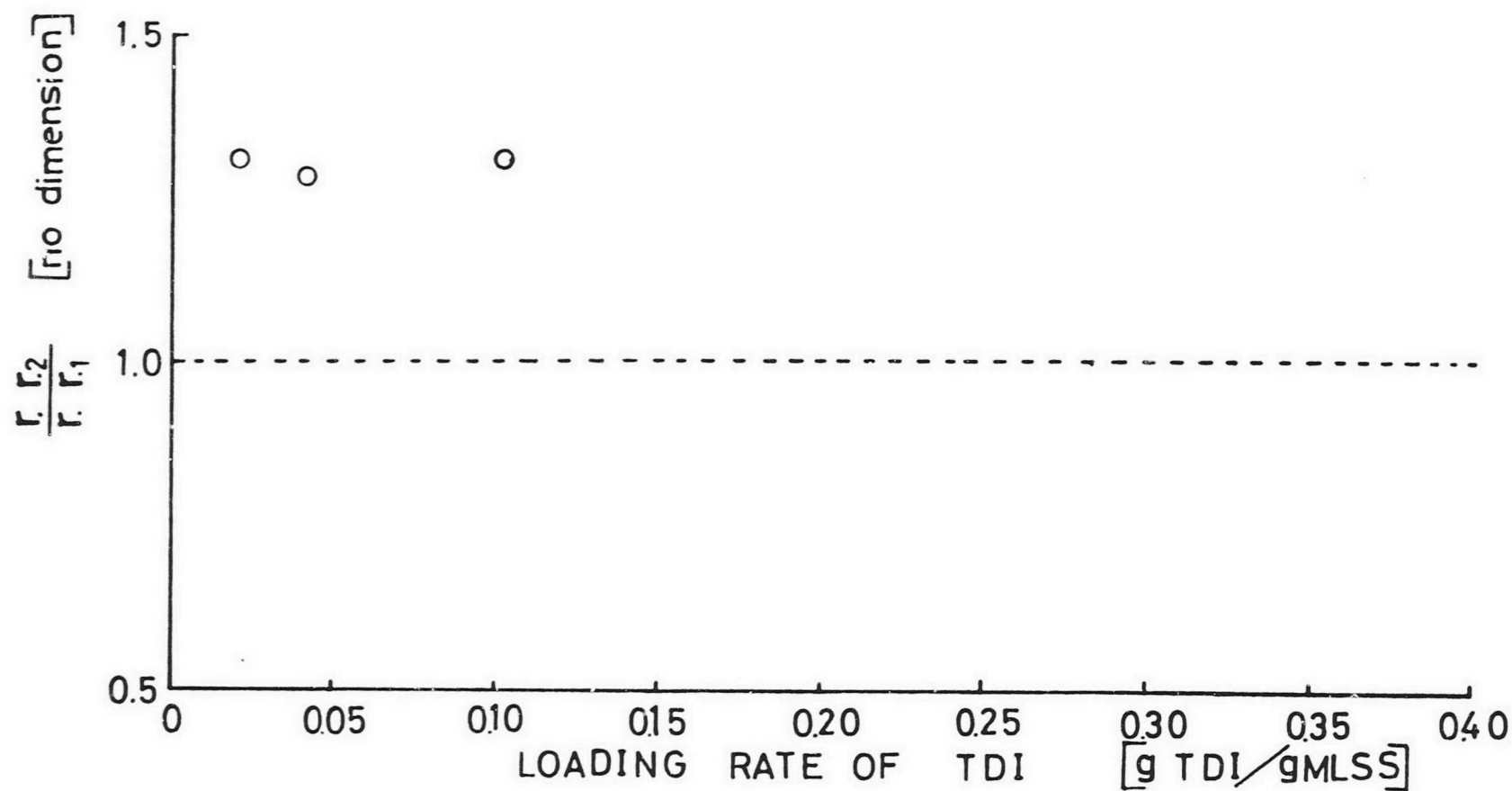r. r.$_2$ ...... RESPIRATION RATE AFTER LOADING

Fig. 5S4-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

5S5-0

DATE 11/21

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	22.0	pH	6.79
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.6	OXIDATION - REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2708	INFLUENT COD (mg/l) COD_{in}	122
SPECIFIC VOLUME SV_{30}	64.8	EFFLUENT COD (mg/l) COD_{eff}	33.9
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	239	REMOVAL EFFICIENCY OF COD (%)	72.2
INFLUENT WATER FLOW RATE (l/day)	193	FOOD:MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	0.089
HYDRAULIC DETENTION TIME (hr^{-1})	12.2	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 5 : 1

Vorticella was active.

Rotifera was not active.

Foamy at surface.

TABLE 5S5-1   RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSly CULTURED ACTIVATED SLUDGE)

ADDED TDI SLUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gMLSS	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	$\dfrac{r. r._2}{r. r._1}$
490	0.181	11.7	9.31	0.79
970	0.358	12.0	7.31	0.61
290	0.107	10.6	9.53	0.90
680	0.251	9.75	7.09	0.73
780	0.288	10.6	7.75	0.73
390	0.144	9.97	9.08	0.91
190	0.0702	11.1	10.6	0.96
97	0.0358	9.97	9.31	0.93
49	0.0181	10.2	9.97	0.98
580	0.214	10.4	8.42	0.81
580	0.251	9.53	7.09	0.74

r. r.$_1$ ······ RESPIRATION RATE BEFORE LOADING

r. r.$_2$ ······ RESPIRATION RATE AFTER LOADING

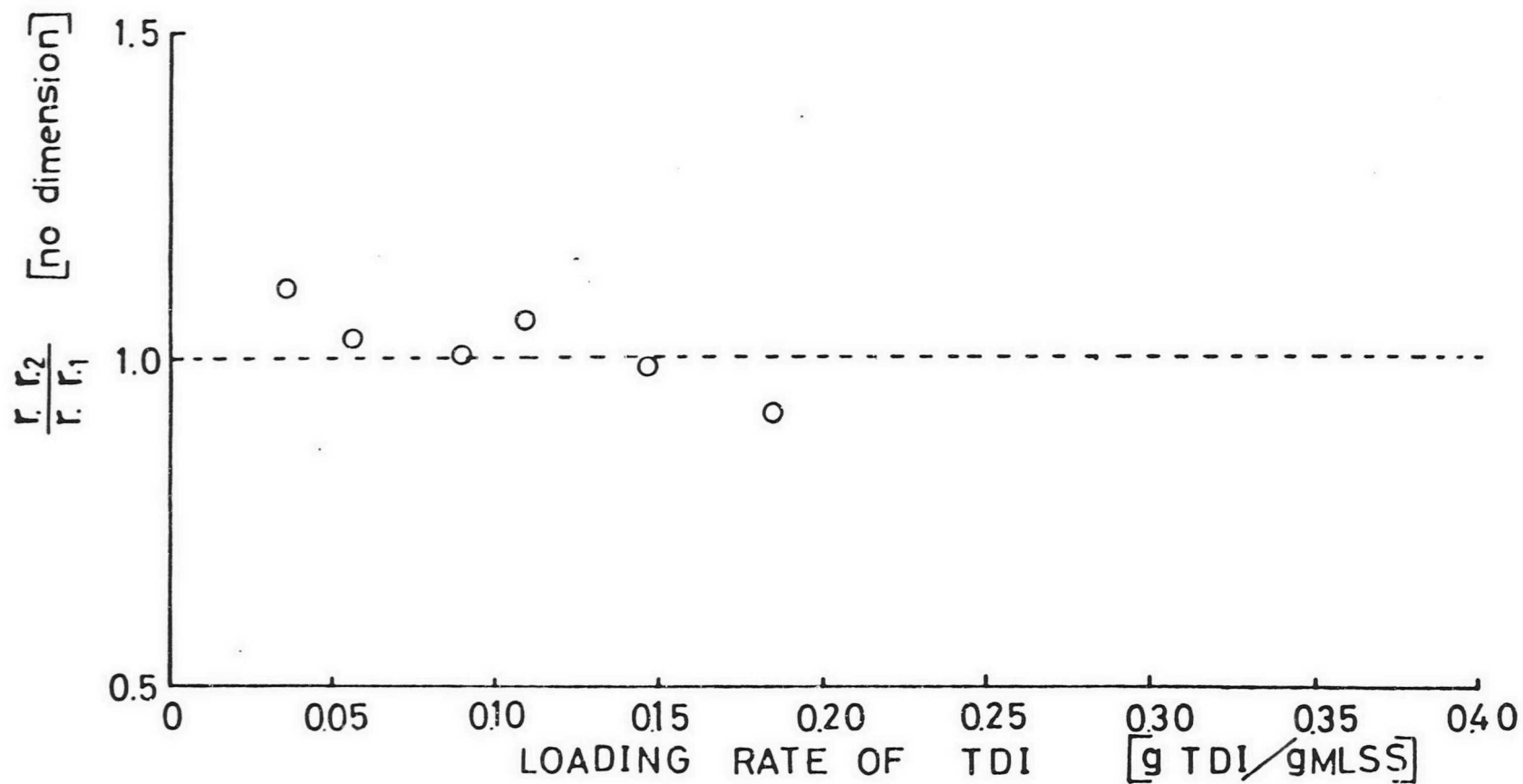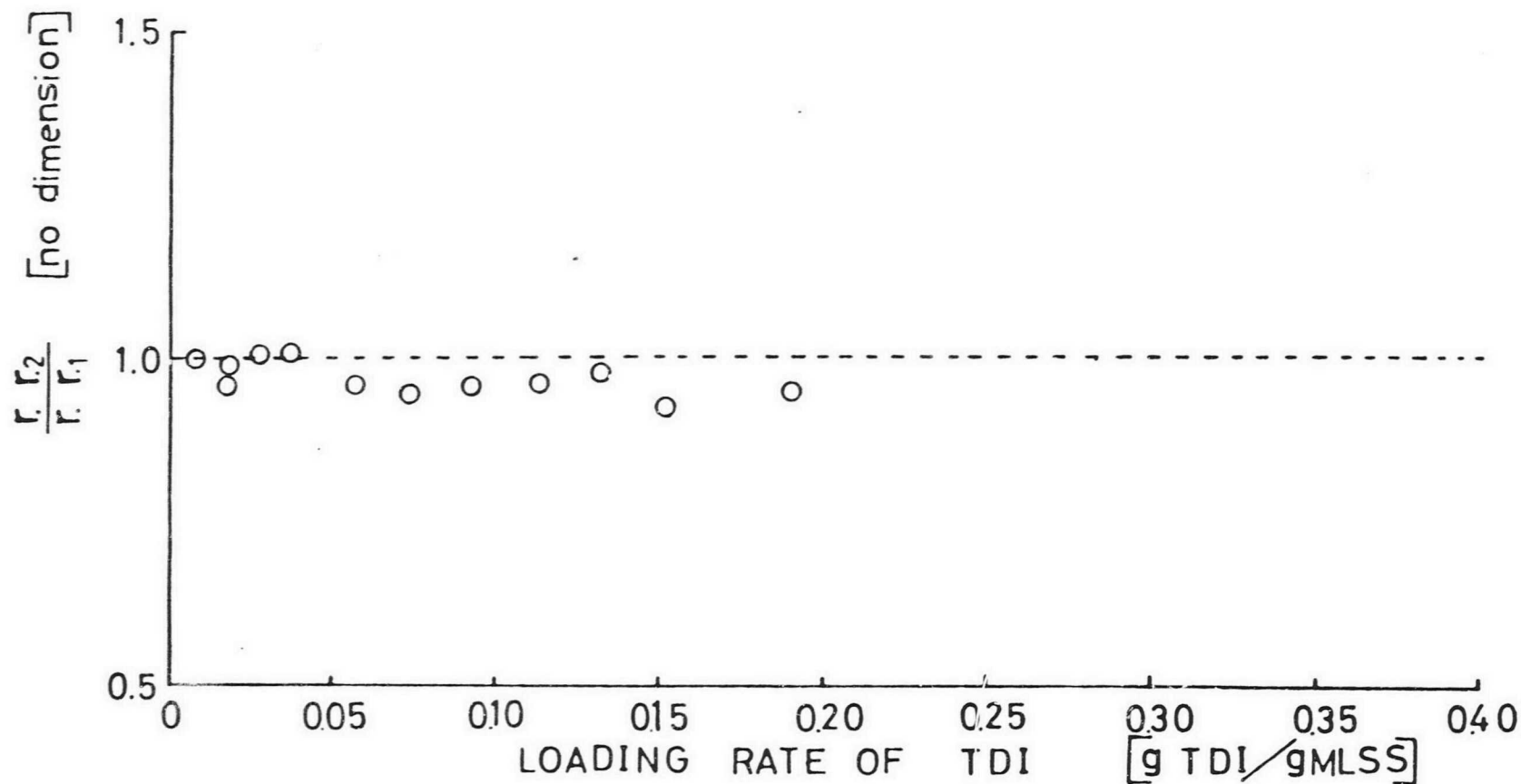**Fig. 5S5-1** RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

5S6-0

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	23.0	pH	5.03
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.8	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2032	INFLUENT COD (mg/l) COD_{in}	45.5
SPECIFIC VOLUME SV_{30}	13.0	EFFLUENT COD (mg/l) COD_{eff}	14.2
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	63.9	REMOVAL EFFICIENCY OF COD (%)	58.8
INFLUENT WATER FLOW RATE (l /day)	230	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	0.053
HYDRAULIC DETENTION TIME (hr^{-1})	10.2	RESPIRATION RATE (mg O_2/ hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 1:5

Vorticella and Rotifera were not active.

Floc was dispersive.

RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

$\dfrac{\text{ADDED TDI}}{\text{SUCTION WEIGHT}}$ ppm	$\dfrac{\text{ADDED TDI}}{\text{MLSS}}$ gTDI/gMLSS	$r.r._1$ mgO$_2$/hr gMLSS	$r.r._2$ mgO$_2$/hr gMLSS	$\dfrac{r.r._2}{r.r._1}$
97	0.0477	13.3	16.0	1.20
240	0.118	16.0	14.8	0.93
150	0.0738	16.3	18.0	1.11
190	0.0935	16.3	18.3	1.13
490	0.241	15.7	16.8	1.08
49	0.0241	18.6	20.7	1.11
240	0.118	17.7	19.5	1.10
390	0.192	16.3	17.1	1.05
290	0.143	14.8	18.3	1.24

$r.r._1$ ...... RESPIRATION RATE BEFORE LOADING

$r.r._2$ ...... RESPIRATION RATE AFTER LOADING

TABLE 5S6-2 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSly CULTURED ACTIVATED SLUDGE)

$\dfrac{\text{ADDED TDI}}{\text{SlUTION WEIGHT}}$ ppm	$\dfrac{\text{ADDED TDI}}{\text{MLSS}}$ gTDI/gMLSS	$r.\,r_1$ mgO$_2$/hr gMLSS	r_2 mgO$_2$/hr gMLSS	$\dfrac{r.\,r_2}{r.\,r_1}$
97	0.0477	18.0	18.6	1.03
240	0.118	16.8	15.7	0.93
150	0.0738	16.0	17.1	1.07
190	0.0935	16.0	17.1	1.07
490	0.241	16.8	12.7	0.75
49	0.0241	21.3	19.5	0.92
240	0.118	17.1	18.6	1.09
390	0.192	18.3	14.8	0.81
290	0.143	17.7	15.1	0.85

$r.\,r_1$ ...... RESPIRATION RATE BEFORE LOADING

$r.\,r_2$ ...... RESPIRATION RATE AFTER LOADING
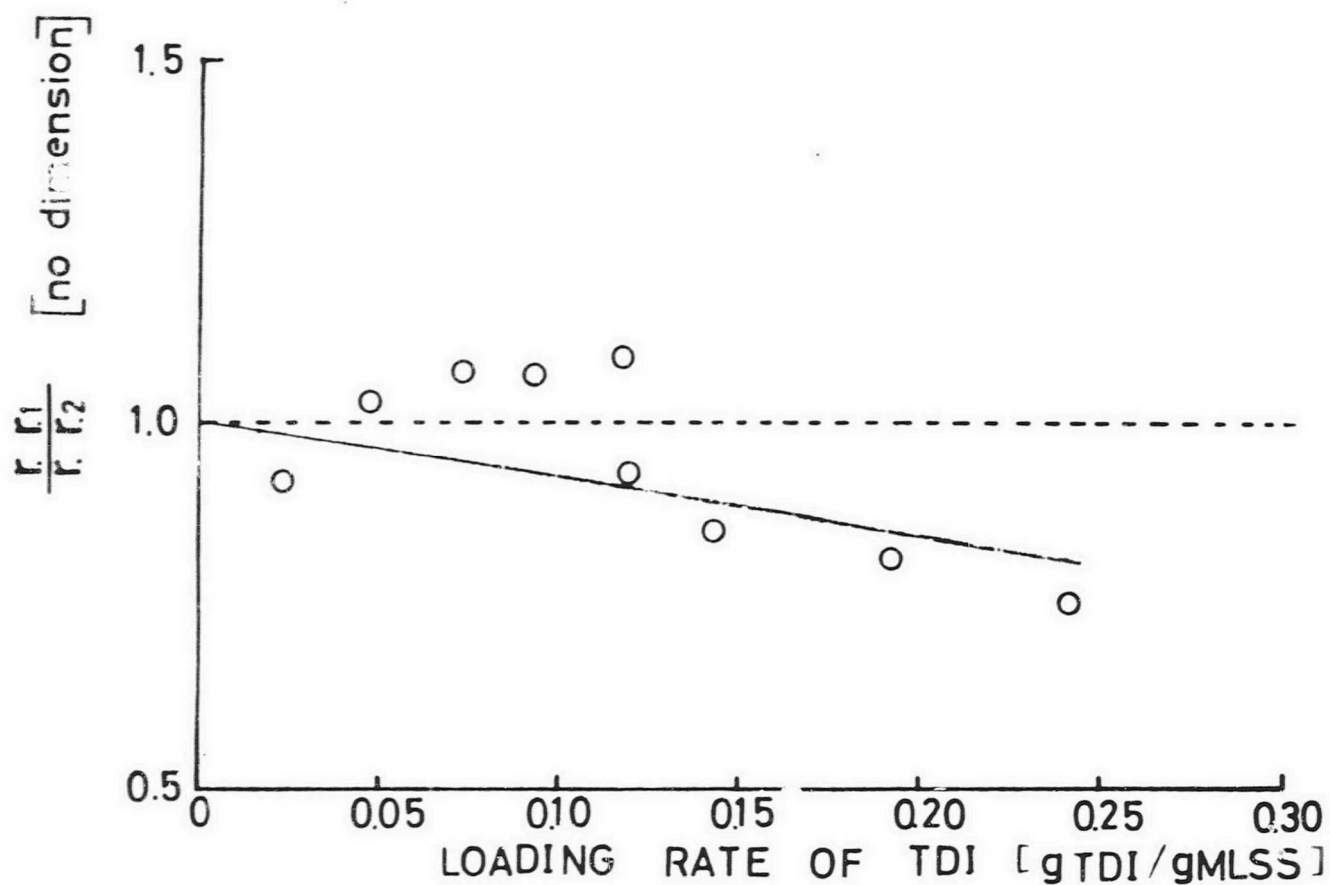
Fig. 5 s 6-1 COMPARISON FOR EFFECT OF ELAPSED
TIME AFTER HYDROLYSIS TDI
(IMMEDIATELY AFTER MIXING)
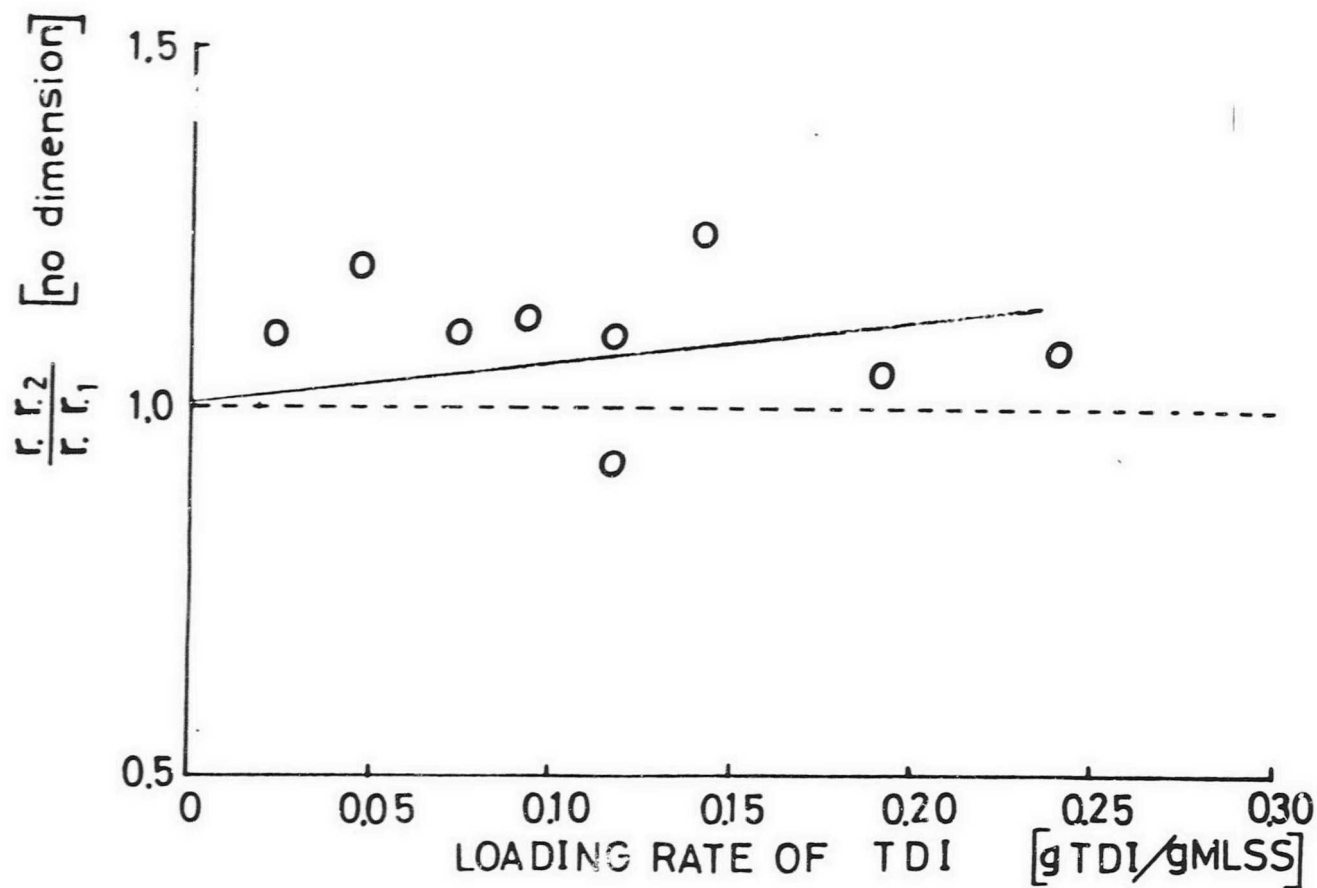
Fig. 5 S 6-2. COMPARISON FOR EFFECT OF ELAPSED
TIME AFTER HYDROLYSIS TDI (2 DAYS.
AFTER MIXING)

DATE 11/30 <u>5S7-0</u>

AERATION TANK No.	IV	LOADING CONDITION	Contin- uous
TEMPERATURE (°C) T	27.0	pH	6.38
DISSOLVED OXYGEN CON- CENTRATION (mg/l) D O	1.0	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1280	INFLUENT COD(mg/l) COD_{in}	92.2
SPECIFIC VOLUME SV_{30}	7.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	54.7	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)	179	FOOD : MICROORGANISM RATIO F/M (gCOD / gMLSS·/)	0.132
HYDRAULIC DETENTION TIME (hr^{-1})	13.1	RESPIRATION RATE (mg O_2 / hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 1:6
  Vorticella and Rotifera were not active.

TABLE 5S7-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (CONTINUOUSLY CULTURED ACTIVATED SLUDGE)

ADDED TDI / SOLUTION WEIGHT ppm	ADDED TDI / MLSS g TDI/gMLSS	r. r_1 mgO$_2$/hr gMLSS	r. r_2 mgO$_2$/hr gMLSS	$\dfrac{r.\ r_2}{r.\ r_1}$
4 DAYS AFTER MIXING				
49	0.0383	13.1	13.1	1.00
360	0.281	15.9	15.0	0.94
730	0.570	14.8	11.7	0.79
1210	0.945	11.3	7.97	0.71
3 DAYS AFTER MIXING				
49	0.0383	14.1	14.1	1.00
360	0.281	13.4	13.4	1.00
730	0.570	14.1	11.7	0.83
1210	0.945	12.2	6.33	0.52
2 DAYS AFTER MIXING				
49	0.0383	15.0	15.0	1.00
360	0.281	15.0	13.4	0.81
730	0.570	15.2	11.5	0.76
1210	0.945	11.3	8.44	0.75
IMMEDIATELY AFTER MIXING				
49	0.0383	11.7	11.7	1.00
360	0.281	13.8	12.4	0.90
730	0.570	14.3	11.3	0.79
1210	0.945	15.7	6.80	0.43
1210	0.945	14.3	7.50	0.52

r. r_1 ------ RESPIRATION RATE BEFORE LOADING

r. r_2 ------ RESPIRATION RATE AFTER LOADING
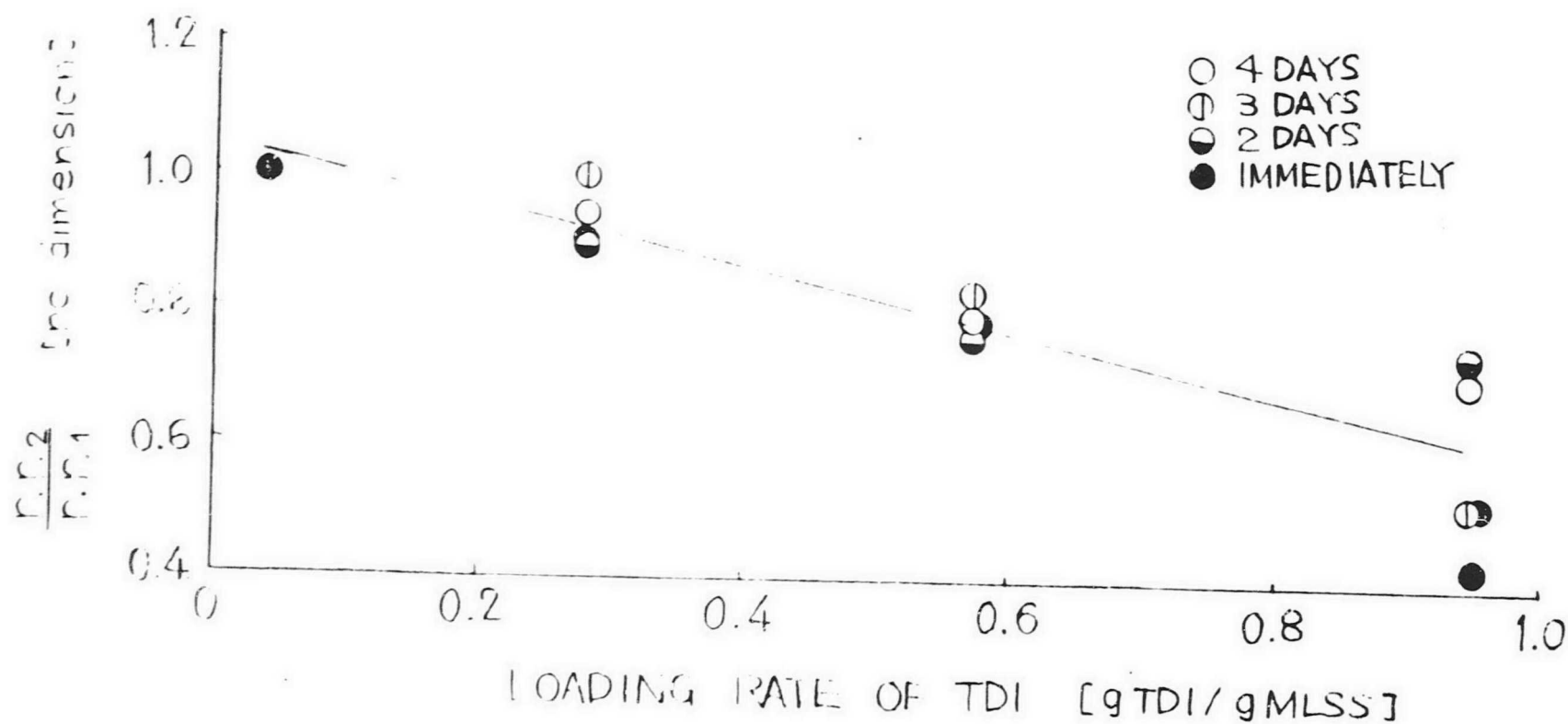
Fig. 5S7-1 COMPARISON FOR EFFECT OF ELAPSED TIME AFTER HYDROLYSIS OF TDI

5S8-0

DATE 11/22

AERATION TANK No.	I	LOADING CONDITION	Without feeding
TEMPERATURE (°C) T		pH	5.39
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO		OXIDATION - REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	954	INFLUENT COD (mg/l) COD_{in}	——
SPECIFIC VOLUME SV_{30}	6.9	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	80.8	REMOVAL EFFICIENCY OF COD (%)	——
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	——
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Verticella was not found.

Rotifera was small and not active.

[Rotifera] = 10

Various kinds of microbes were found.

Flock was dispersive.

Aeration has been continued for 4 days.

TABLE 5S8-1 | RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI

(ENDOGENOUS)

ADDED TDI SLUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gMLSS	$r \cdot r_1$ mgO₂/hr gMLSS	$r \cdot r_2$ mgO₂/hr gMLSS	$\dfrac{r \cdot r_2}{r \cdot r_1}$
1210	1.42	4.92	4.92	1.00
240	0.281	5.67	6.67	1.00
120	0.141	5.27	5.27	1.00
1210	1.42	6.67	6.67	1.00
61	0.0714	5.62	4.57	0.81
610	0.714	6.32	4.92	0.78
850	0.995	5.27	5.62	1.07

$r \cdot r_1$ ······ RESPIRATION RATE BEFORE LOADING

$r \cdot r_2$ ······ RESPIRATION RATE AFTER LOADING
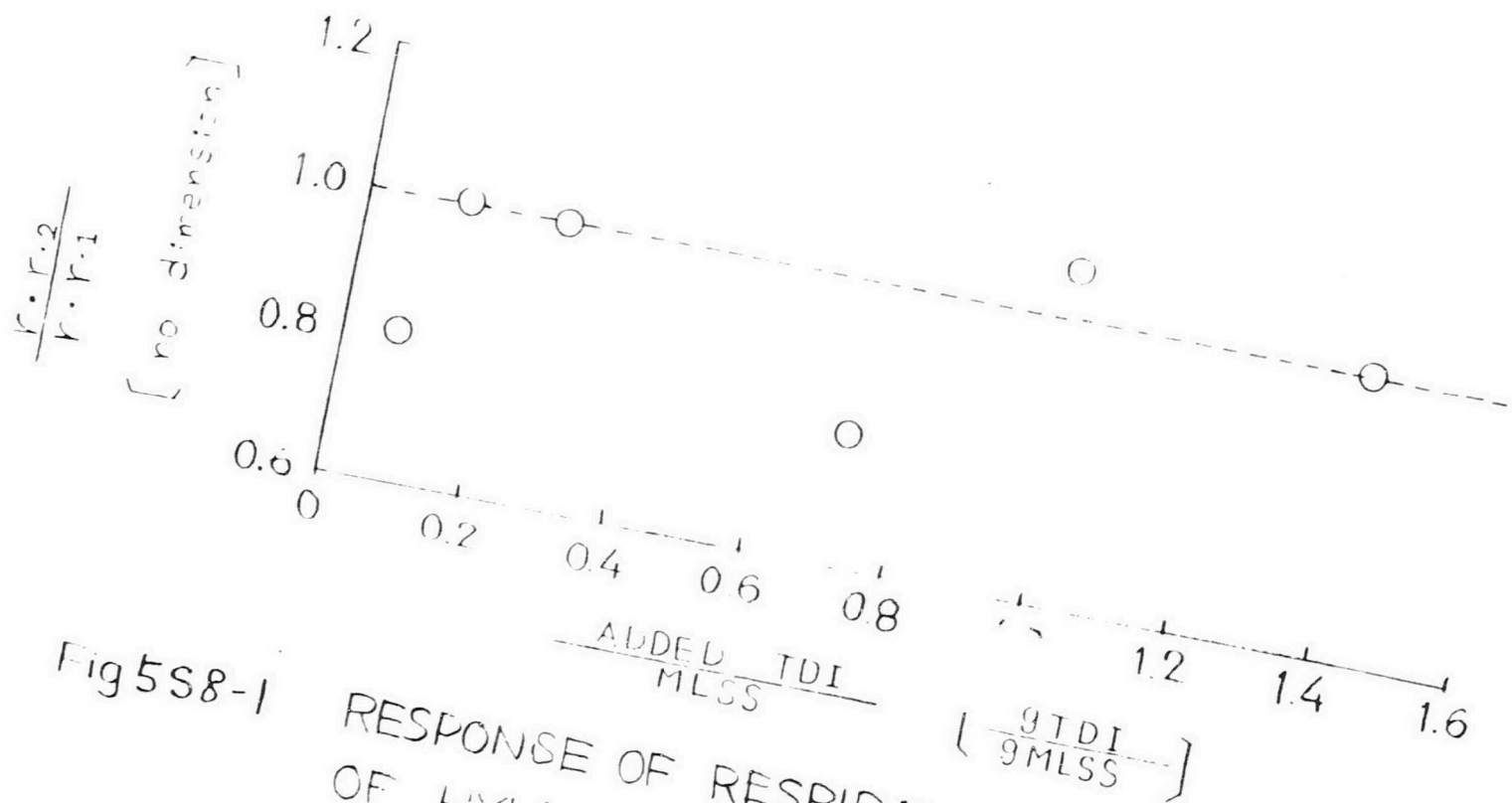
Fig 5S8-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (ENDGENOUS)

DATE 11/26

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	5.98
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1380	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	6.5	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	47.1	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F/M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 4 : 3

Vorticella and Rotifera were active.

Table 5S9-1

TIME min	pH	r. r$_1$ mgO$_2$/hr gMLSS	r. r$_2$ mgO$_2$/hr gMLSS	$\frac{r. r_2}{r. r_1}$
0	5.98	7.39	6.96	0.94
1	4.80			
2	4.64	7.83		
6	5.10	10.9	12.2	1.12
14	5.40	10.9	13.0	1.20
22	5.70	12.6	12.6	1.00
37	6.07	14.8	14.8	1.00
55	6.24	13.0	13.0	1.00
80	6.46	10.9	13.0	1.19
115	6.70	11.3	12.2	1.08
156	6.81	13.0	13.0	1.00
184	6.90	12.6		
213	6.89	10.4	11.7	1.13
230	6.87	10.0	11.3	1.13
260	6.84	9.78	9.13	0.93
290	6.84	11.3	11.3	1.00
336	6.66	9.57	10.0	1.04

r. r$_1$ ------ RESPIRATION RATE BEFORE LOADING

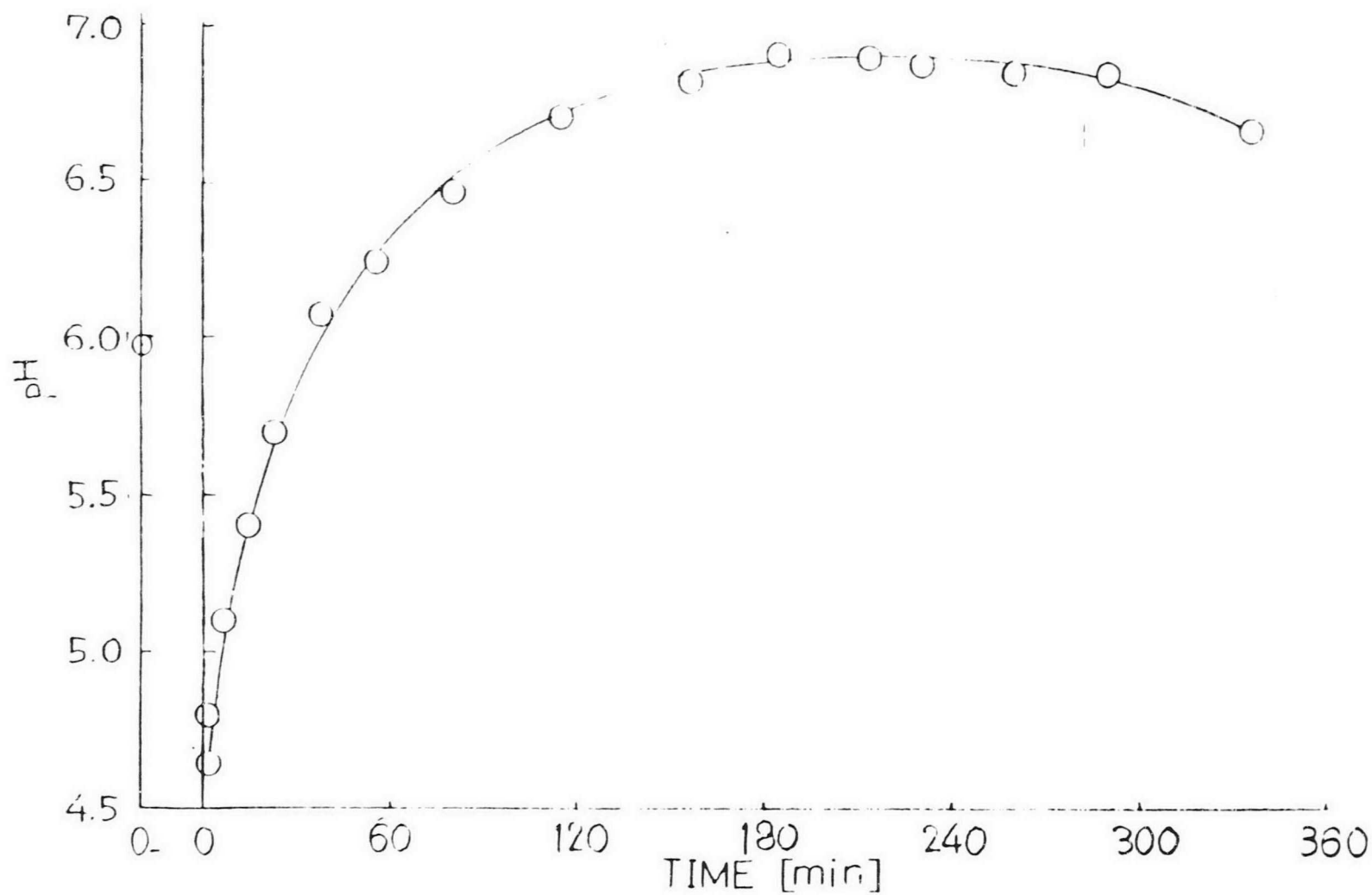r. r$_2$ ------ RESPIRATION RATE AFTER LOADING

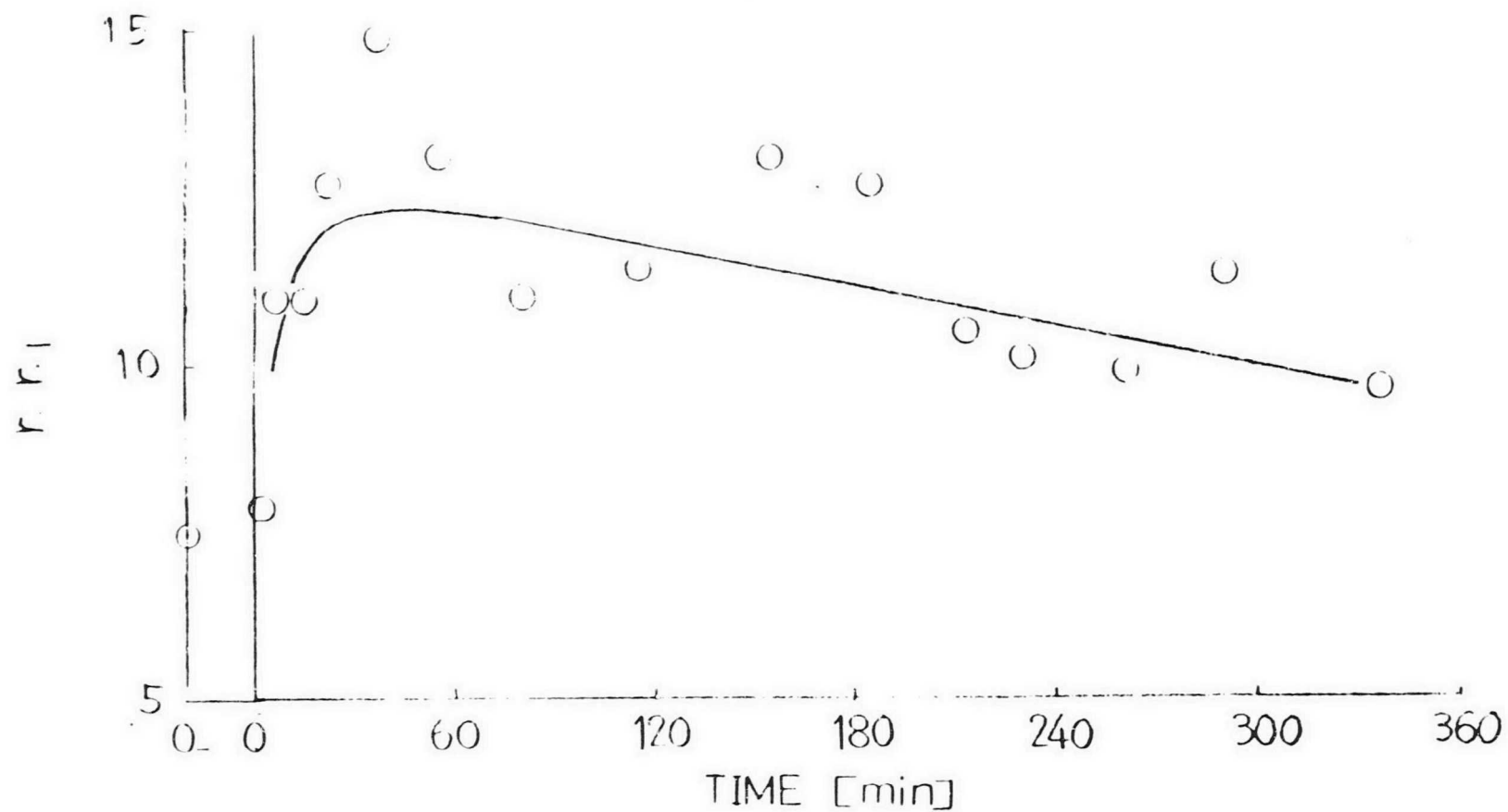Fig.5S9-1 pH CHANGE AFTER ADDITION OF CSL.
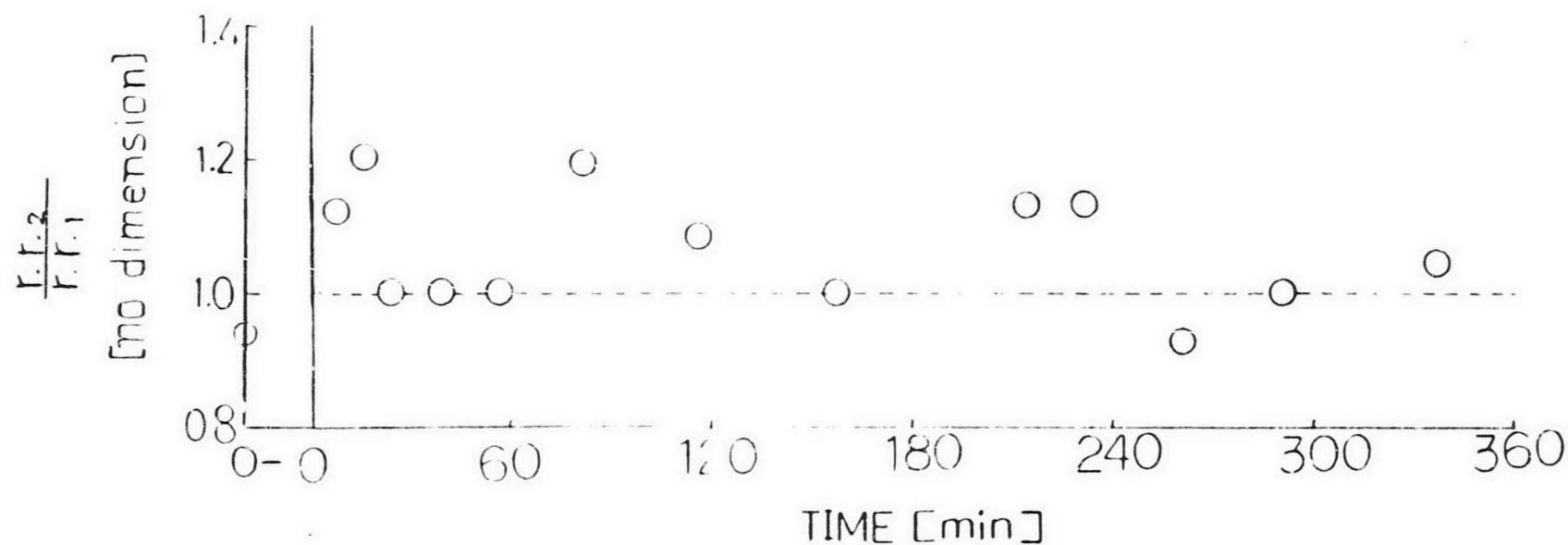
Fig. 559-2. CHANGE OF R.R.1 AFTER ADDITION OF CSL.

Fig. 5S9-3   CHANGE OF R.R. RATIO AFTER ADDITION OF CSL

Fig 5S9-4   DIFFERENCE IN RESPIRATION RATE RATIO
WITH RESPIRATION RATE OF ACTIVATED
SLUDGE SOLUTION
(LOADING RATE OF TDI = 0.040 CgTDI/gMLSS]

DATE 11/25

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	6.98
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1101	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	10.9	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	99.3	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l/day)		FOOD: MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 5 : 5

Flock was massive.

TABLE 5S10-1

TIME min	pH	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	$\dfrac{r.\ r._2}{r.\ r._1}$
0.	6.98	5.72	6.27	1.10
2	6.24	48.0	43.6	0.91
8	6.30	52.3	46.9	0.90
16	6.40	45.8		
27	6.62	41.4		
41	6.71	44.7		
54	6.87	49.0		
73	7.00	49.0		
88		39.2	39.2	1.00
115		40.3		
135		33.8		
163		32.7	31.6	0.97
201		18.5	19.6	1.06
210		19.6		
246		13.1	14.2	1.08
279		10.9	11.4	1.05

r. r.$_1$ ------ RESPIRATION RATE BEFORE LOADING
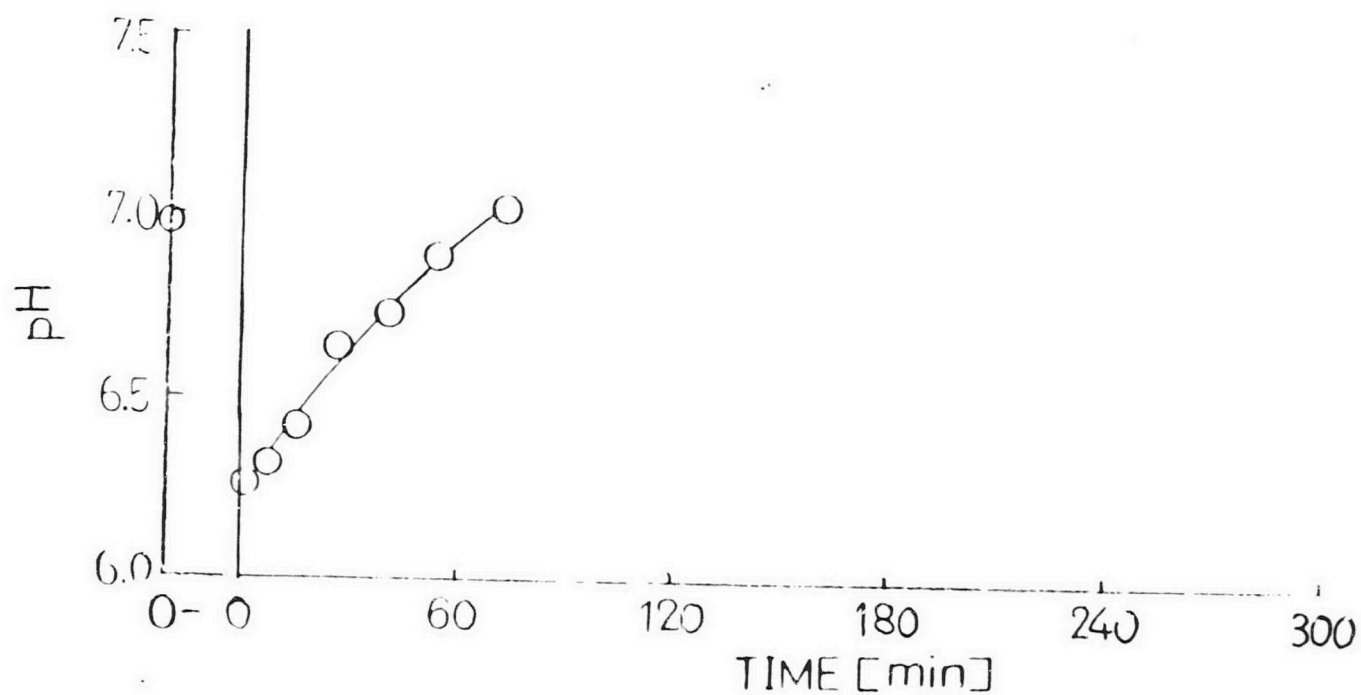
r. r.$_2$ ------ RESPIRATION RATE AFTER LOADING

Fig5S10-1 pH CHANGE AFTER ADDITION OF CSL.
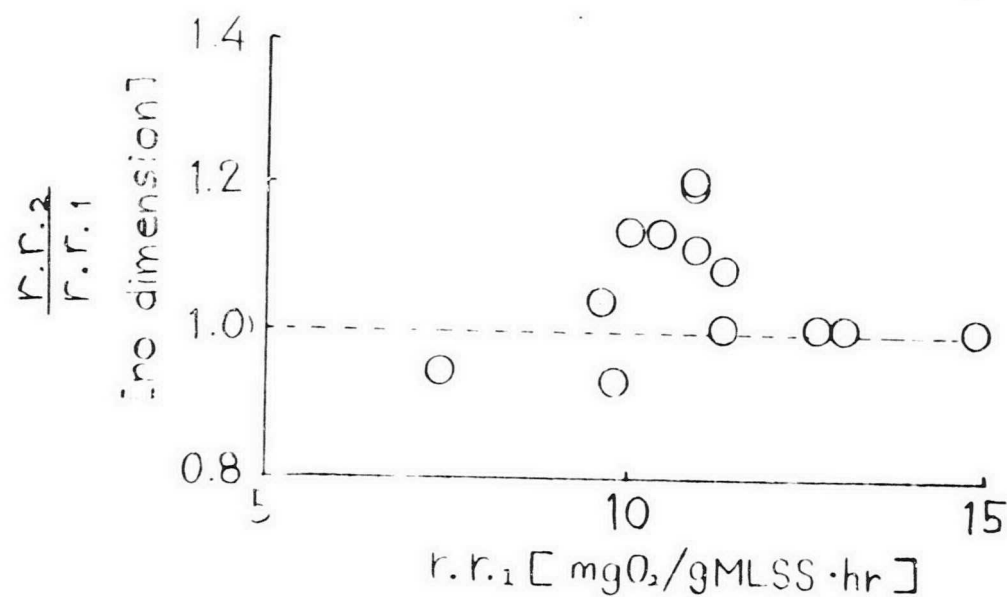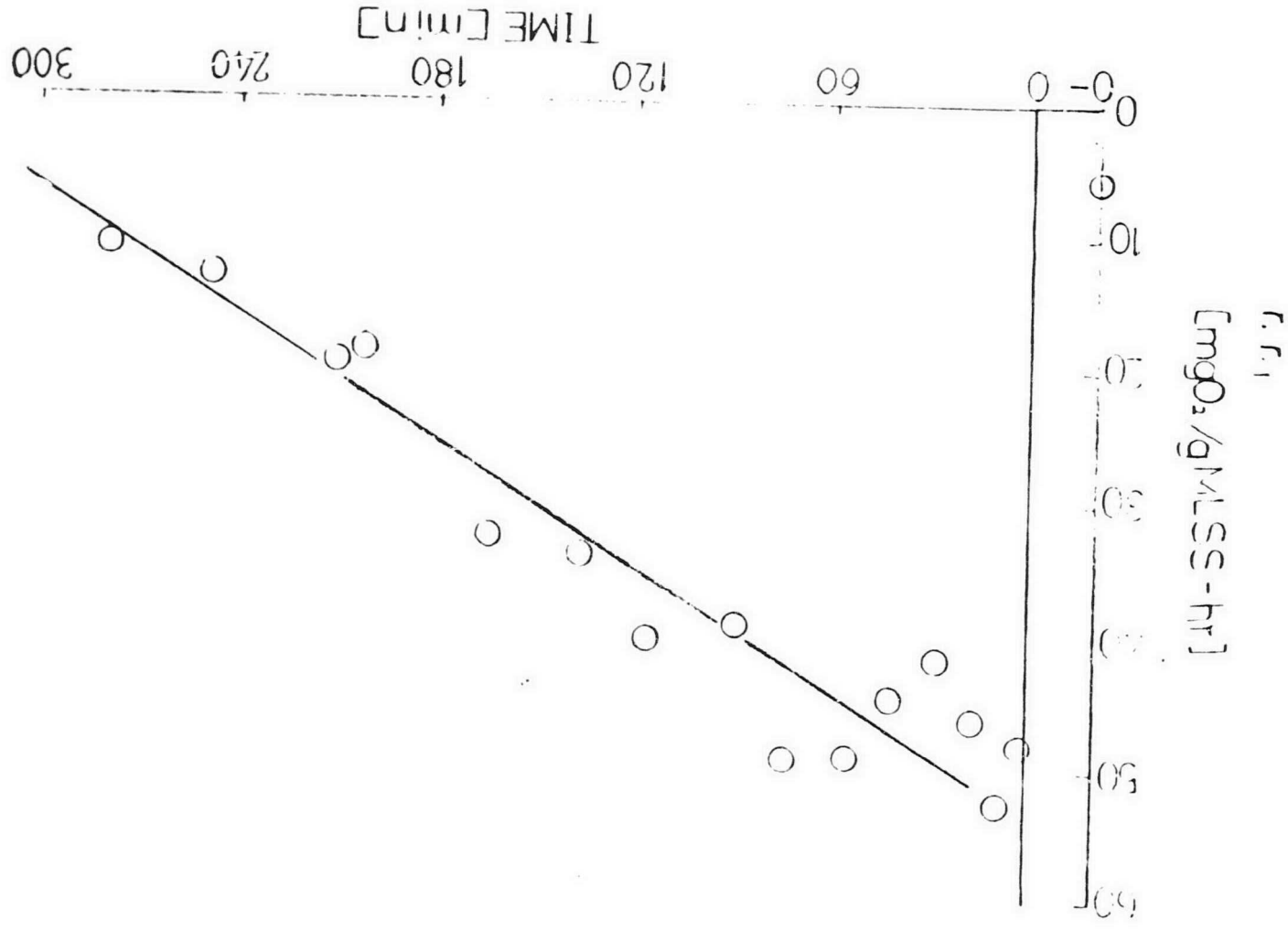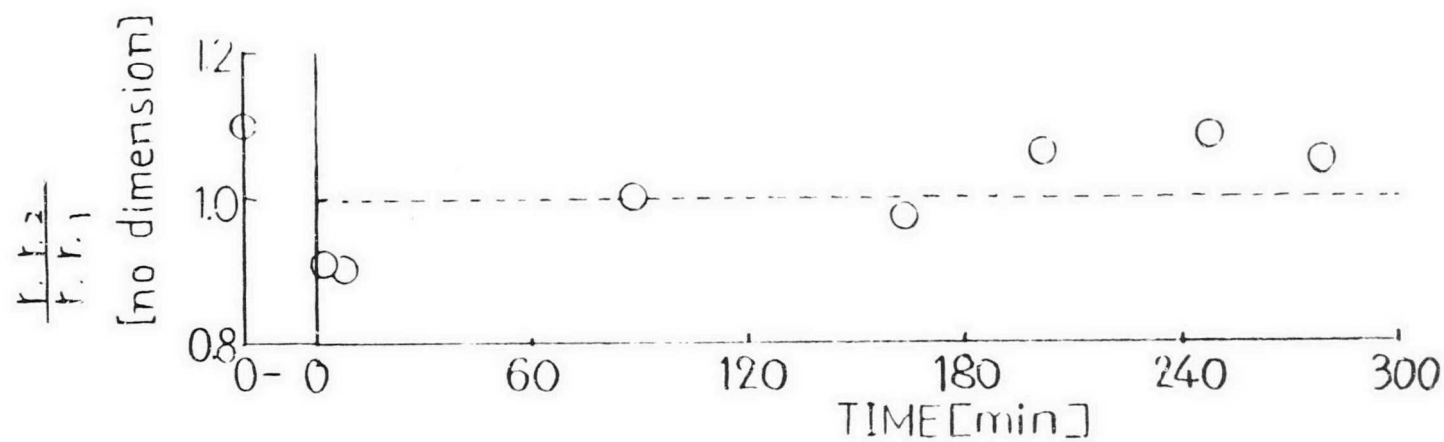
Fig 5S10-3 CHANGE OF R.R. RATIO AFTER ADDITION OF CSL
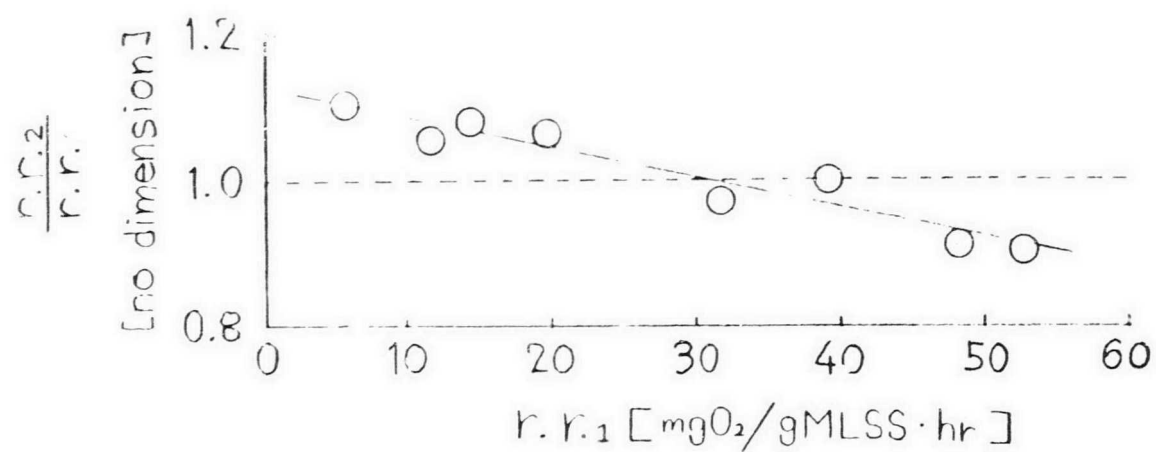
Fig 5S10-4 DIFFERENCE IN RESPIRATION RATES RATIO
WITH RESPIRATION RATE OF ACTIVATED
SLUDGE SOLUTION
(LOADING RATE OF TDI = 0.661 [gTDI/gMLSS])

DATE

AERATION TANK No.	I	LOADING CONDITION	Batch
TEMPERATURE (°C) T		pH	6.24
DISSOLVED OXYGEN CON- CENTRATION (mg/l) DO		OXIDATION - REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	838	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	5.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	59.7	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was slightly found.

[Rotifera] = 5~10 , Av. 6
Rotifera was active.

TABLE 5S11-1

TIME min	pH	r. r_1 mgO$_2$/hr gMLSS	r. r_2 mgO$_2$/hr gMLSS	$\dfrac{r. \ r_2}{r. \ r_1}$
0-	6.24	15.4	6.44	0.42
1	4.90	19.3	8.23	0.43
14	5.39	23.3	9.31	0.40
27	5.60	25.4		
46	6.00	32.2	15.8	0.49
90	6.40	29.7	10.4	0.35
121	6.42	22.2	11.1	0.50
152	6.47	15.2	5.61	0.37
182	6.48	14.4	4.77	0.33

r. r_1 ······ RESPIRATION RATE BEFORE LOADING

r. r_2 ······ RESPIRATION RATE AFTER LOADING

Fig5SII-I pH CHANGE AFTER ADDITION OF CSL.

Fig 5S11-2 CHANGE OF R.R.1 AFTER ADDITION OF CSL.

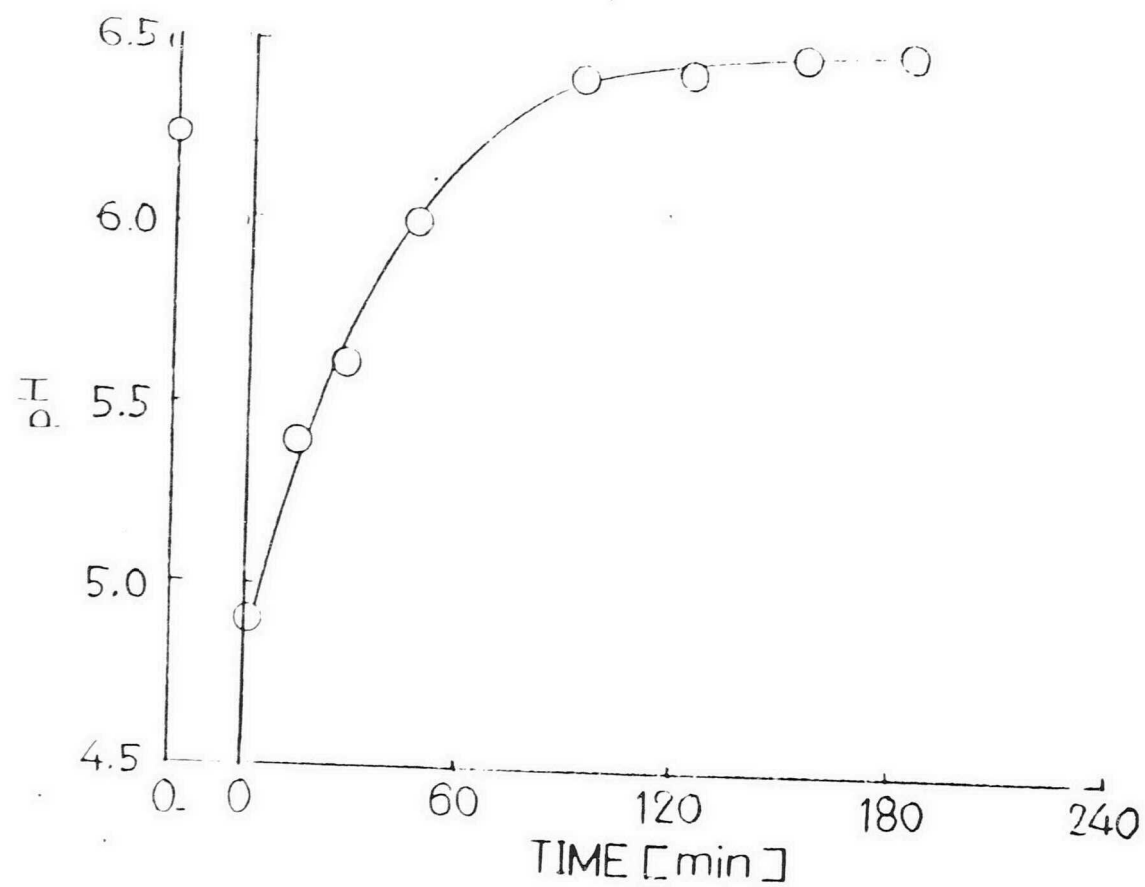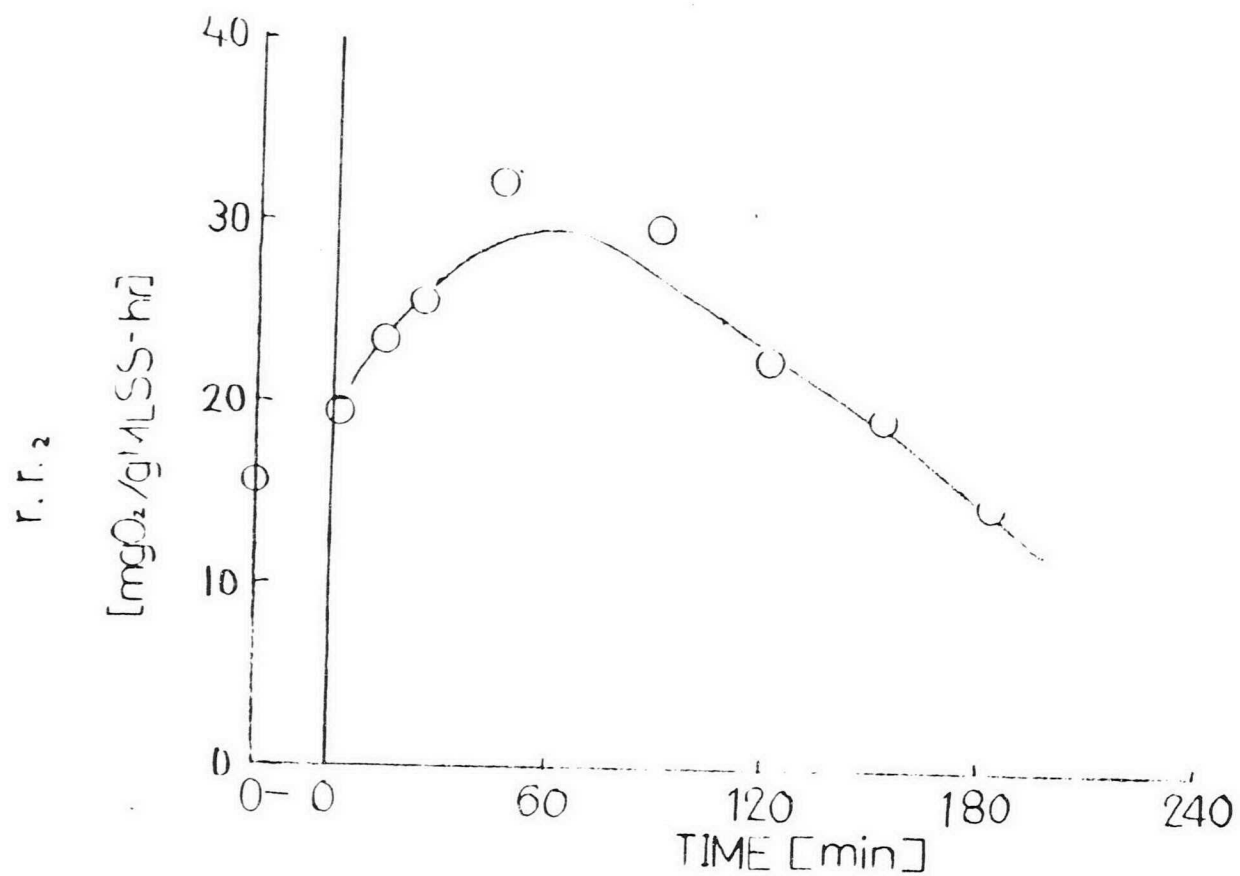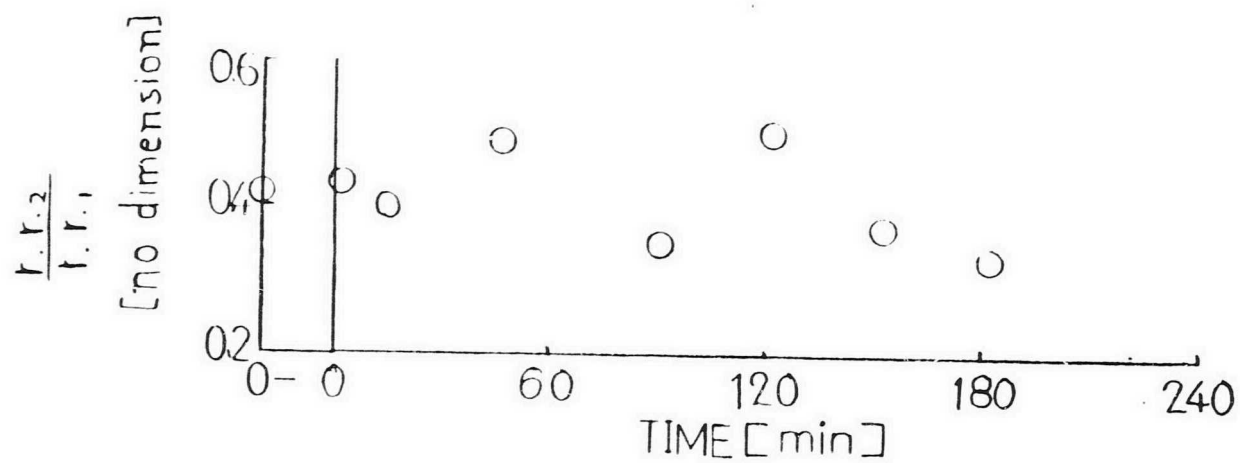Fig. 5S11-3 CHANGE OF R.R. RATIO AFTER ADDITION OF CSL
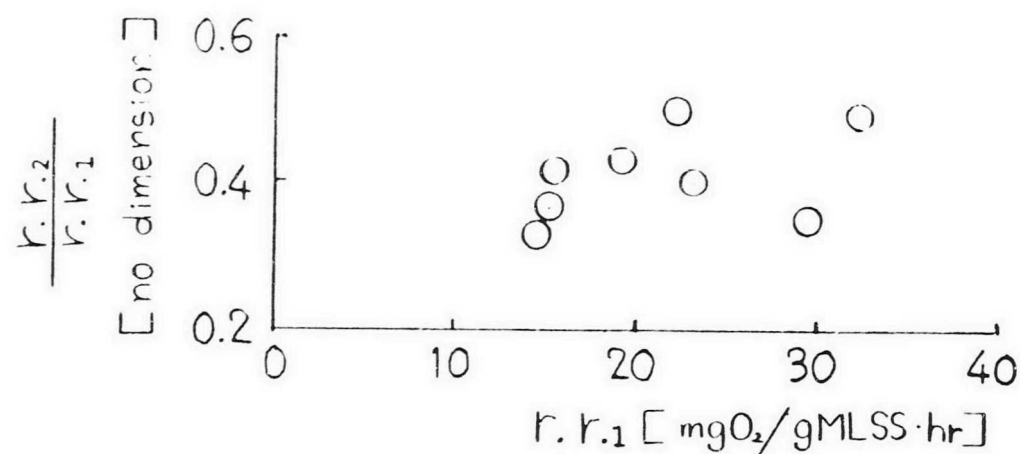
Fig. 5S11-4   DIFFERENCE IN RESPIRATION RATE RATIO
WITH RESPIRATION RATE OF ACTIVATED
SLUDGE SOLUTION
(LOADING OF TDI = 1.45 [gTDI/g MLSS])

DATE 11/15   5S12 - 0

AERATION TANK No.	V	LOADING CONDITION	Excess loading
TEMPERATURE (°C) T		pH	4.50
DISSOLVED OXYGEN CON- CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2636	INFLUENT COD(mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}	23.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	92.7	REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)	—	FOOD: MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})	—	RESPIRATION RATE (mg O_2 / hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella and Rotifera were not found.

TABLE 5S12-1   RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI   (EXCESS SUBSTRATE FEEDING)

ADDED TDI SLUTION WEIGHT ppm	ADDED TDI MLSS g TDI/gM·SS	r.r.$_1$ mgO$_2$/hr gMLSS	r.r.$_2$ mgO$_2$/hr gMLSS	$\dfrac{r.r._2}{r.r._1}$
490	0.185	9.79	7.97	0.81
340	0.129	7.97	7.74	0.97
240	0.0911	6.60	6.83	1.03
150	0.0569	7.06	7.97	1.15
49	0.0186	6.83	7.29	1.07

r.r.$_1$ ······ RESPIRATION RATE BEFORE LOADING

r.r.$_2$ ······ RESPIRATION RATE AFTER LOADING

The above values were plotted in Fig. 5S13-1.

DATE 11/15

AERATION TANK No.	V	LOADING CONDITION	Excess loading
TEMPERATURE (°C) T		pH	4.45
DISSOLVED OXYGEN CON- CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	2658	INFLUENT COD (mg/l) COD_{in}	
SPECIFIC VOLUME SV_{30}		EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI		REMOVAL EFFICIENCY OF COD (%)	
INFLUENT WATER FLOW RATE (l /day)	—	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	
HYDRAULIC DETENTION TIME (hr^{-1})	—	RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella and Rotifera were not found

TABLE 5S13-1 RESPONSE OF RESPIRATION RATE TO ADDITION OF HYDROLYZED TDI (EXCESS SUBSTRATE FEEDING)

ADDED TDI / SLUTION WEIGHT ppm	ADDED TDI / MLSS g TDI/gMLSS	r. r.$_1$ mgO$_2$/hr gMLSS	r. r.$_2$ mgO$_2$/hr gMLSS	r. r.$_2$ / r. r.$_1$
150	0.0564	5.87	6.32	1.08
240	0.0903	6.21	6.32	1.02
340	0.128	8.47	9.03	1.07

r. r.$_1$ ······ RESPIRATION RATE BEFORE LOADING

r. r.$_2$ ······ RESPIRATION RATE AFTER LOADING
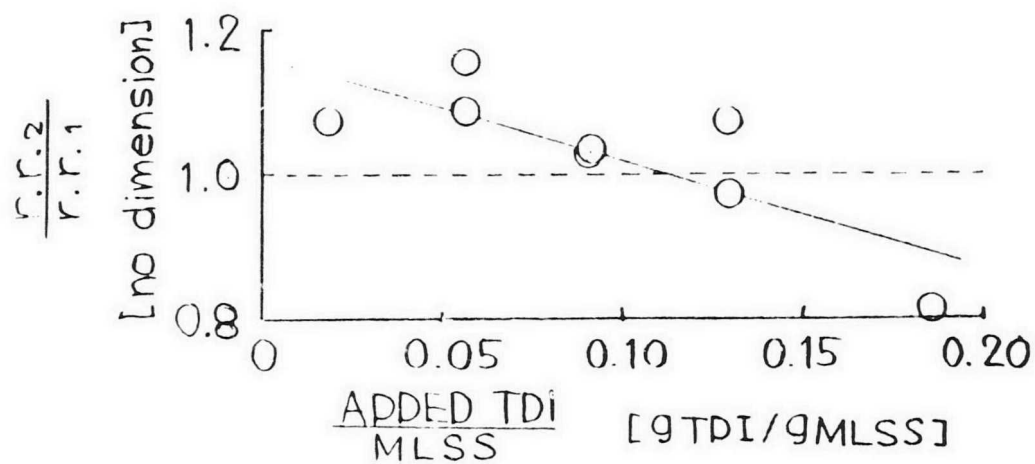
Fig. 5S13-1   RESPONSE OF RESPIRATION RATE TO ADDITION
OF HYDROLYZED TDI (EXCESS SUBSTRATE
FEEDING)

TABLE 5.1

CORRELATION OF DEPENDENCY OF RESPIRATION RATE RATIO ON ADDITION OF HYDROLYZED TDI WITH SVI AND EFFLUENT COD

$S = \dfrac{(r.\ r.\ ratio)}{\left(\substack{\text{Loading rate of} \\ \text{hydrolyzed TDI}}\right)}$ $\left[\dfrac{gMLSS}{gTDI}\right]$	S V I	Effluent COD ppm
1.2	48.7	13.2
0	106	27.3
0	97.1	—
1.1	239	33.9

Fig. 5-1.   CORRELATION OF RESPIRATION ACTIVITY
WITH SVI FOR CONTINUOUS CULTURED
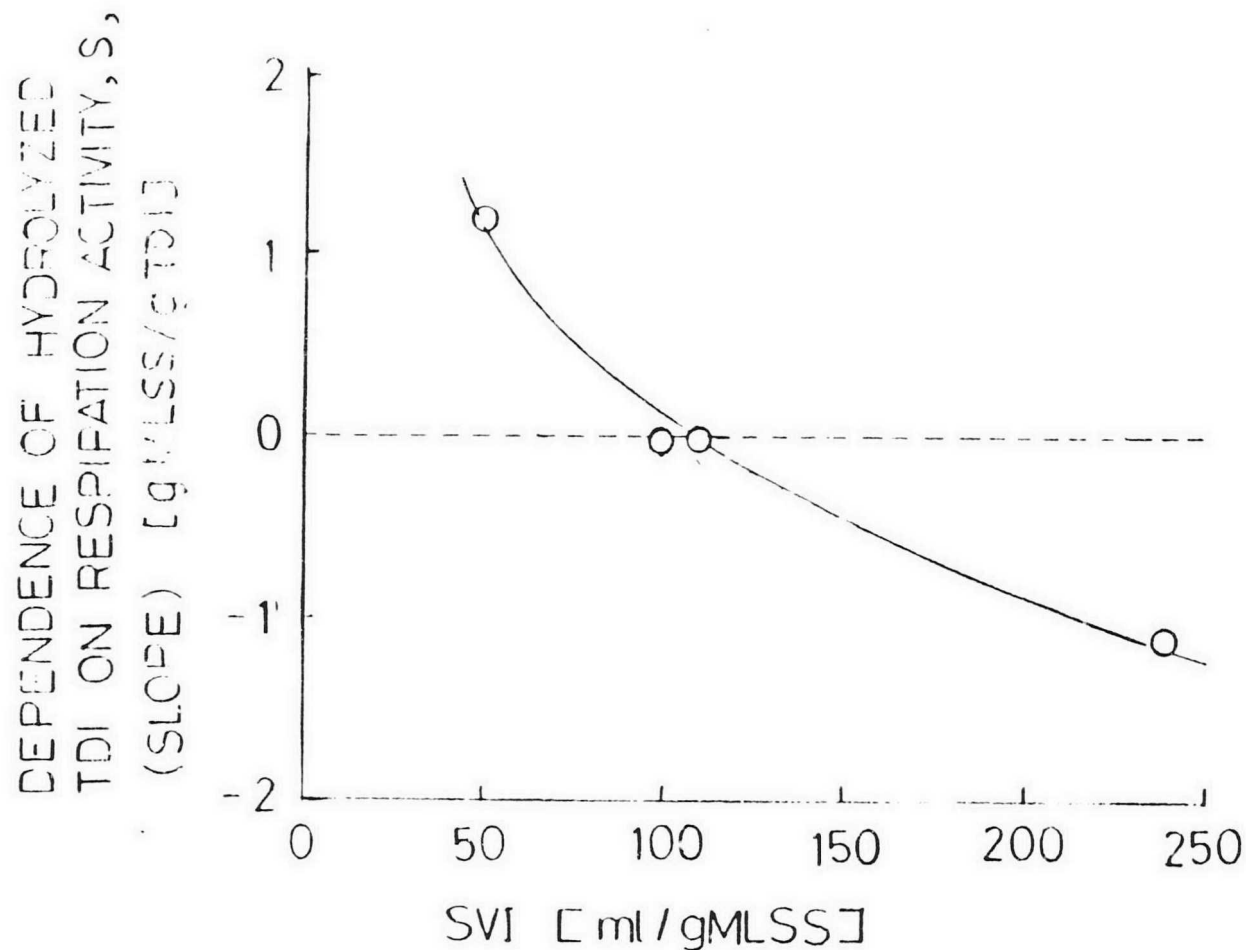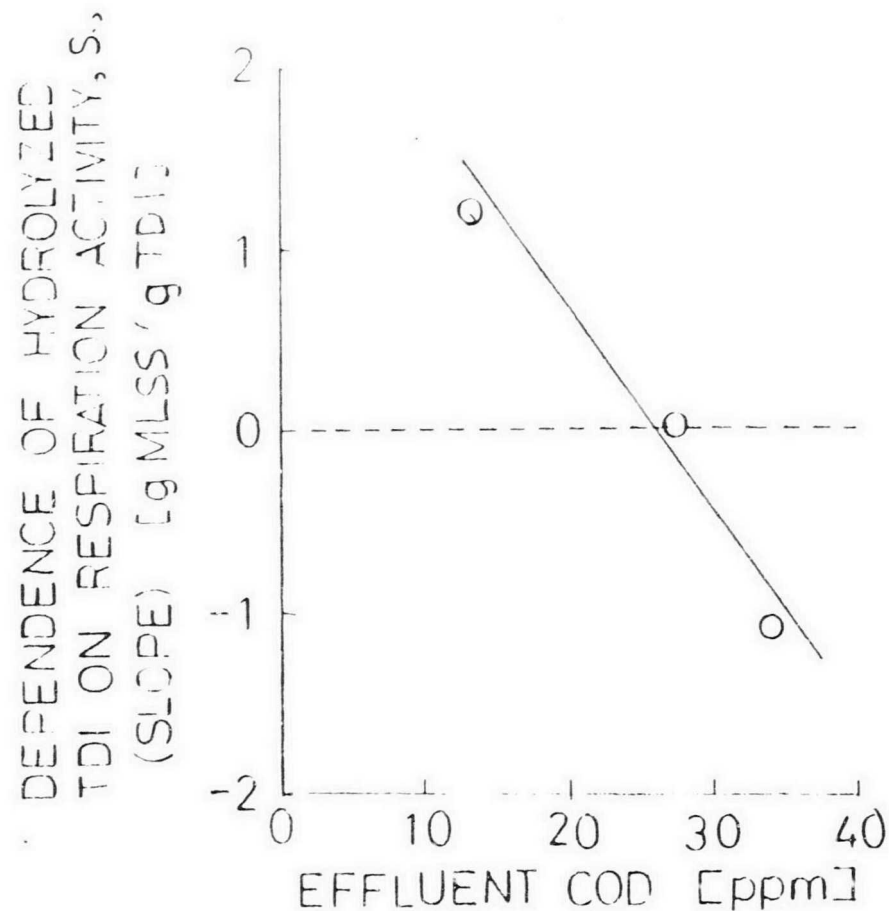ACTIVATED SLUDGE SOLUTION

Fig. 5.-2. CORRELATION OF RESPIRATION ACTIVITY WITH EFFLUENT COD FOR CONTINUOUS CULTURED ACTIVATED SLUDGE SOLUTION

6.   The Response of Activated Sludge to Triethylene Diamine

6.1   Introduction

Triethylene diamine is soluble into water.

If it is mixed in the TDI vapour, it would be absorbed
with water in a scrubber as well as TDI. Thus, the impact
of its solution upon aqua-ecosystem should be investigated.
This chapter described the effect of triethylene diamine
(TED) on the activated sludge. The biological activity
was evaluated by measuring the respiration rate in the
same manner as before.

6.2   Experimental

The experimental procedure was approximately same as that
in Chapter 4. The activated sludge of 200 - 250 ml was
taken from the culture vessel and used as a sample.
The temperature of the experimental vessel was kept
$25 \pm 1^{o}C$.

The activated sludge was aerated at first to elevate DO
up to about 7 mg/L, and then it was insulated suddenly
from the air. The respiration rate was measured from the
slope of decaying curve. During the course of decaying
DO, an amount of TED solution was added.
The respiration rates before and after the addition were
measured.

The respiration rate before the addition was denoted with r.r.1 and that after the addition with r.r.2.

The solutions added contained triethylene diamine of 8.52, 9.85, and 15.2%. The volume of solution added did not exceed 10 ml.

6.3 Results

6.3.0 The number of tables and figures

A few kinds of experiments were conducted by using the activated sludge under the same conditions.
Accordingly, the numbers of table and figure were given as a set as shown below.

```
6 SY - X
```

— Number of chapter

— Set number for experiment

— Number of table or figure in the set
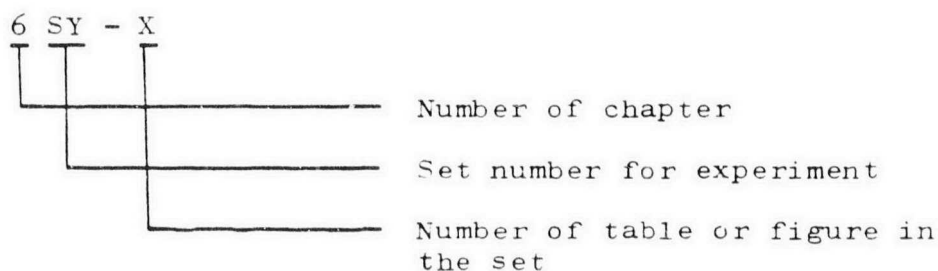
This expression was same as given in the preceding chapters. The tables for X = 0 such as 6S2-0 and 6S5-0 include the biological data.

6.3.1 Change in respiration rate with addition of TED

The activated sludge was cultured in the different ways. The experiments of 6S1-X, 6S2-X, and 6S3-X were done for the activated sludges of continuous culture.

The figures of 6SY-1 (Y = 1, 2, and 3) give the plots
between $r.r._2/r.r._1$ and loading rate of TED.

The loading rate was calculated by dividing the amount of
added TED by MLSS of activated sludge.

In figures of 6SY-2 (Y = 1, 2, and 3) $r.r.$ /$r.r.$ was
plotted against the logarithm of loading rate.

The maximum was observed in these plots.

In the plots of $r.r._2$ /$r.r._1$ against the logarithm of load-
ing rate, the peak could be recognized more clearly. It
appeared at the loading rate of 0.7 to 0.8 (g TED/g MLSS).

The value of $r.r._2/r.r._1$ maximum was about 1.5.

In the experiments 6S4-X, the activated sludge cultured
under over-loaded conditions was used.

The relation between $r.r._2/r.r._1$ and loading rate of TED
resembled that obtained before.

The plot showed the maximum of $r.r._2/r.r._1 = 1.5$ at the
loading rate of 0.5 (g·TED/g·MLSS).

The experiments for 6S5-X and 6S6-X were done with the
activated sludge under endogenous conditions.

The activated sludge was aerated without feeding the
substrate until the endogenous condition was attained.

The plots of $r.r._2/r.r._1$ against loading rate of TED did
not give the peak. $r.r._2/r.r._1$ decreased at the high

loading rate.

- The relation $r.r._2/r.r._1 > 1$ held for the loading of TED less than 2 $(g \cdot TED/g \cdot MLSS)$.

6.4 Discussions

In each experiment the respiration was accelerated with triethylene diamine as long as its loading rate was less than 2 $(g \cdot TED/g \cdot MLSS)$. In other words triethylene diamine could be an substrate for the activated sludge cultured with corn steep liquor.

However, when the loading rate exceeded 2 $(g \cdot TED/g \cdot MLSS)$ TED acted as an inhibitor.

The most favourable condition for the treatment would be the loading rate of 0.5 + 0.08 $(g \cdot TED/g \cdot MLSS)$.

6.5. Conclusion

(1) Triethylene diamine accelerated the respiration rate of the activated sludge as long as loading rate of TED was less than 2 $(g-TED/G \cdot MLSS)$ regardless of the conditions of culture.

(2) $r.r._2/r.r._1$ attained maximum at the loading rate of 0.5 tp 0.8($g \cdot TED/g \cdot MLSS$)

Thus, the most faborable treatment would be expected at the above loading rate.

DATE 12/3

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	24.0	pH	6.39
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.4	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1504	INFLUENT COD(mg/l) COD_{in}	73.5
SPECIFIC VOLUME SV_{30}	8.0	EFFLUENT COD (mg/l) COD_{eff}	15.0
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	53.2	REMOVAL EFFICIENCY OF COD (%)	79.6
INFLUENT WATER FLOW RATE (l /day)	177	FOOD:MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	0.064
HYDRAULIC DETENTION TIME (hr^{-1})	13.3	RESPIRATION RATE (mg O_2/ hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 3 : 3
Hyphomycetes were found.

TABLE 651-1

Effect of T E D solution on respiration rate of activated
sludge system (CONTINUOUS FEEIDING)

TED CONC. ppm	Loading rate gTED/gMLSS	$r.r_1$ $\dfrac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\dfrac{mgO_2}{hr\,gMLSS}$	$\dfrac{r.r_1}{r.r_2}$
3390	2.25	11.6	11.2	0.97
3390	2.25	9.97	9.77	0.98
2040	1.36	10.8	11.8	1.09
1360	0.904	10.2	12.4	1.22
2720	1.81	9.18	9.57	1.04
680	0.452	9.97	12.4	1.24
1700	1.13	9.57	11.0	1.15
1020	0.678	10.6	12.6	1.19
340	0.226	13.0	14.8	1.14

$r.r_1$ ······· respiration rate before loading

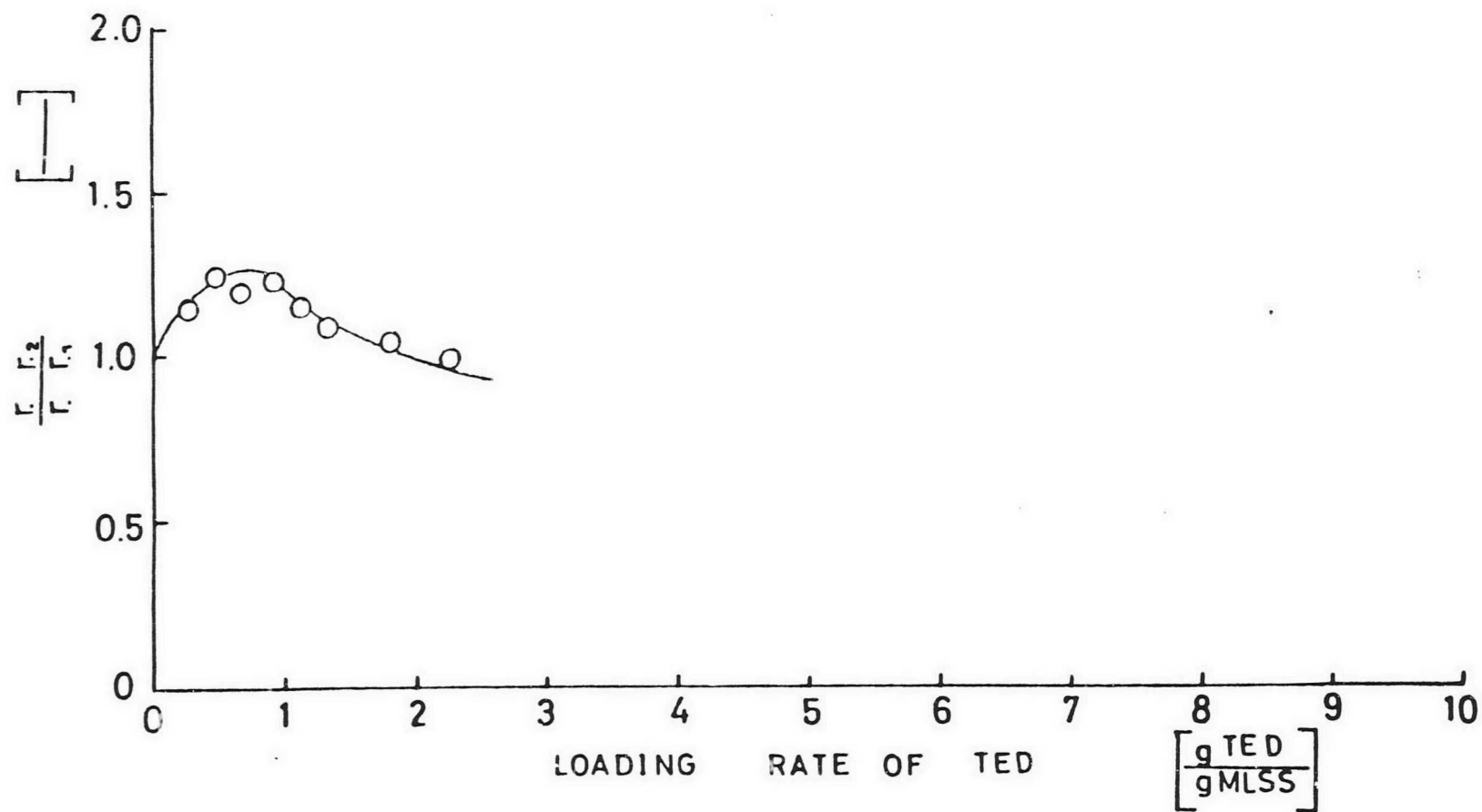$r.r_2$ ······ respiration rate after loading

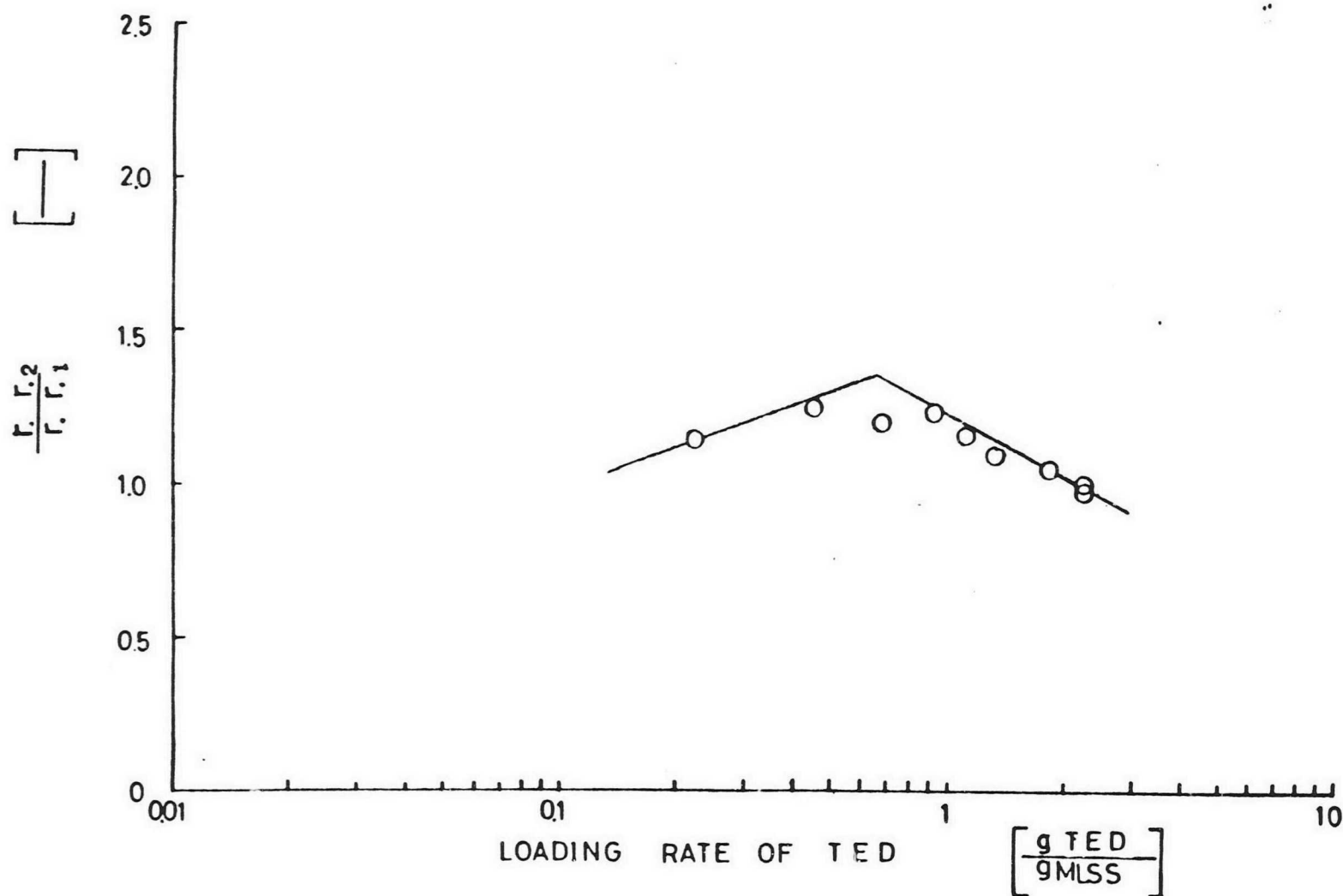Fig. 6S1-1   EFFECT OF TED ON ACTIVATED SLUDGE
(CONTINUOUS FEEDING)

Fig. 6S/-2   EFFECT OF   TED   ON   ACTIVATED   SLUDGE
(CONTINUOUS   FEEDING)

DATE 12/5

AERATION TANK No.	IV	LOADING CONDITION	Contin-uous
TEMPERATURE (°C) T	25.2	pH	6.52
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO	0.6	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1512	INFLUENT COD (mg/l) COD_{in}	87.2
SPECIFIC VOLUME SV_{30}	9.5	EFFLUENT COD (mg/l) COD_{eff}	17.5
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	62.8	REMOVAL EFFICIENCY OF COD (%)	79.9
INFLUENT WATER FLOW RATE (l /day)	183	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	0.101
HYDRAULIC DETENTION TIME (hr^{-1})	12.9	RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vortice..a was not found.

[Rotifera] = 2

Hyphomycetes were found.

TABLE 6S2-1

Effect of TED solution on respiration rate of activated sludge system CONTINUOUS FEEDING

TED ppm	Loading rate g TED /gMLSS	r. r.$_1$ $\frac{mgO_2}{hr\,gMLSS}$	r. r.$_2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.\,r._1}{r.\,r._2}$
3790	2.51	12.5	14.3	1.14
7560	5.00	13.3	10.7	0.81
1520	1.01	11.7	15.5	1.32
760	0.503	10.5	18.8	1.79
2280	1.51	14.3	17.9	1.25
5300	3.51	9.92	10.7	1.08
300	0.198	11.9	13.9	1.17
570	0.377	10.3	13.9	1.35
1140	0.754	10.5	13.5	1.28
760	0.503	10.3	14.7	1.42
950	0.629	9.72	14.9	1.53

r. r.$_1$ ...... respiration rate before loading

r. r.$_2$ ...... respiration rate after loading
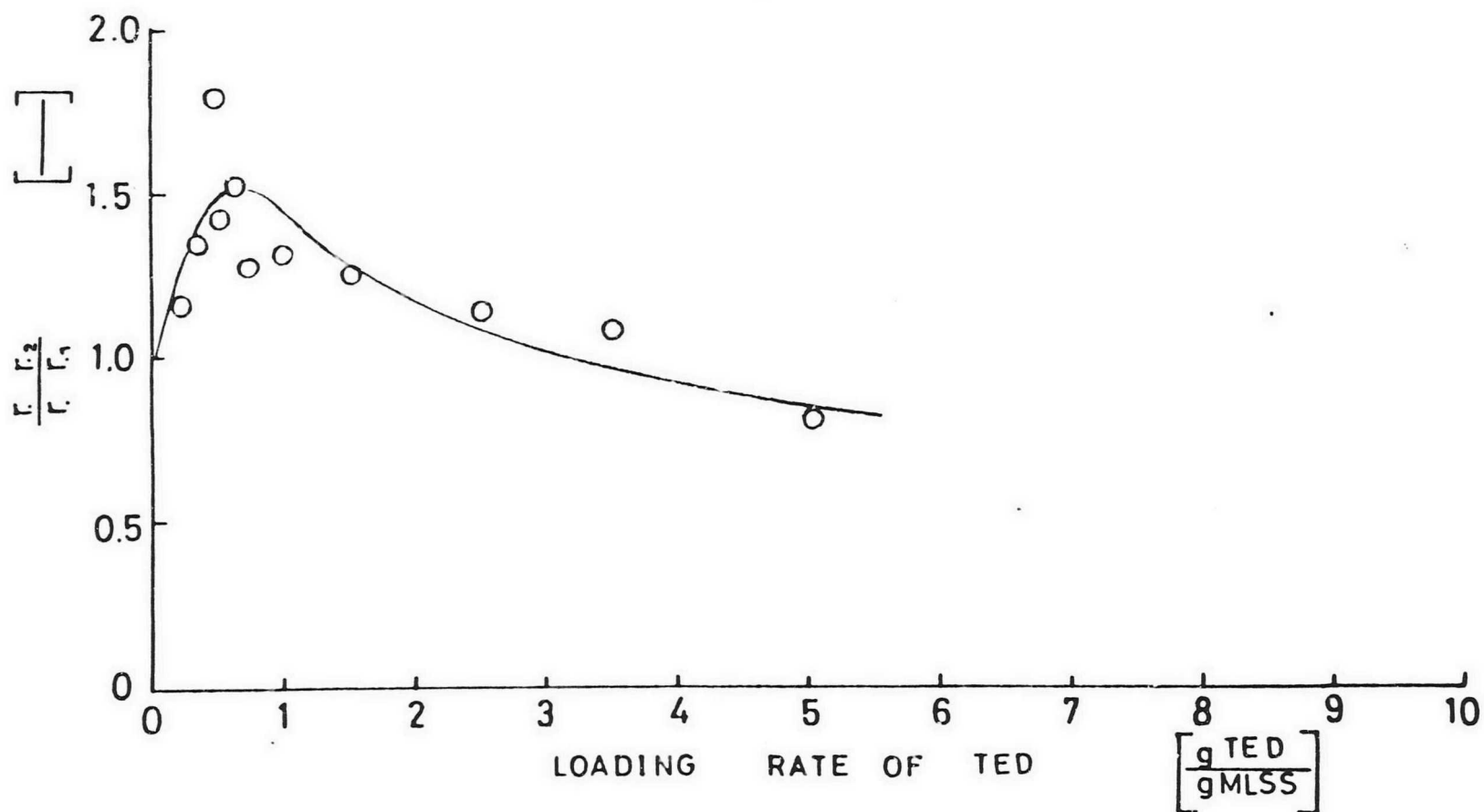
- 283 -

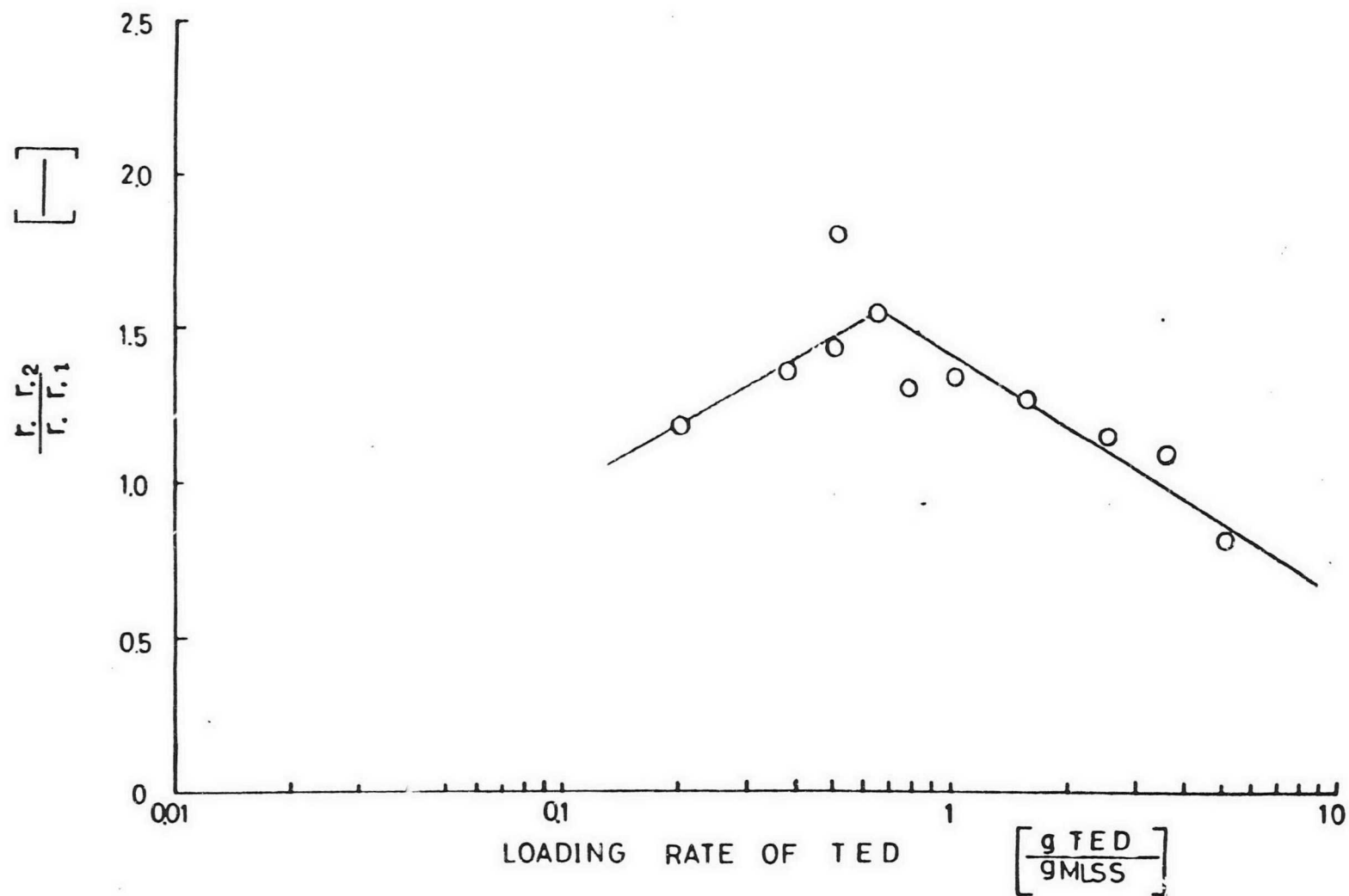Fig. 6S2-1   EFFECT OF TED ON ACTIVATED SLUDGE

(CONTINUOUS FEEDING)

Fig. 6S 2-2 EFFECT OF TED ON ACTIVATED SLUDGE
(CONTINUOUS FEEDING)

DATE 12/6

AERATION TANK No.	IV	LOADING CONDITION	Continuous
TEMPERATURE (°C) T	25.0	pH	6.41
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO	0.5	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1348	INFLUENT COD(mg/l) COD_{in}	71.8
SPECIFIC VOLUME SV_{30}	11.0	EFFLUENT COD (mg/l) COD_{eff}	16.6
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	81.6	REMOVAL EFFICIENCY OF COD (%)	76.9
INFLUENT WATER FLOW RATE (l /day)	169	FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	0.092
HYDRAULIC DETENTION TIME (hr^{-1})	14.0	RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

TABLE 6 3-1

Effect of TED solution or. respiration rate of activated sludge system (CONTINUOUS FEEDING)

TED CONC. ppm	Loading rate gTED /gMLSS	r. r.$_1$ $\frac{mgO_2}{hr\ gMLSS}$	r. r.$_2$ $\frac{mgO_2}{hr\ gMLSS}$	$\frac{r.\ r._1}{r.\ r._2}$
2940	2.18	11.6	12.2	1.06
490	0.364	13.1	17.1	1.31
4900	3.64	12.2	11.4	0.93
980	0.727	10.9	15.6	1.43
3920	2.91	10.9	10.7	0.98
1970	1.46	11.1	14.0	1.26
200	0.148	10.7	14.0	1.31
740	0.549.	11.1	15.6	1.40
9740	7.22	12.2	7.12	0.58
1470	1.09	12.2	15.6	1.27
74	0.0549	10.9	11.6	1.06
1180	2.875	11.1	13.5	1.22

r. r.$_1$ ⋯⋯ respiration rate before loading
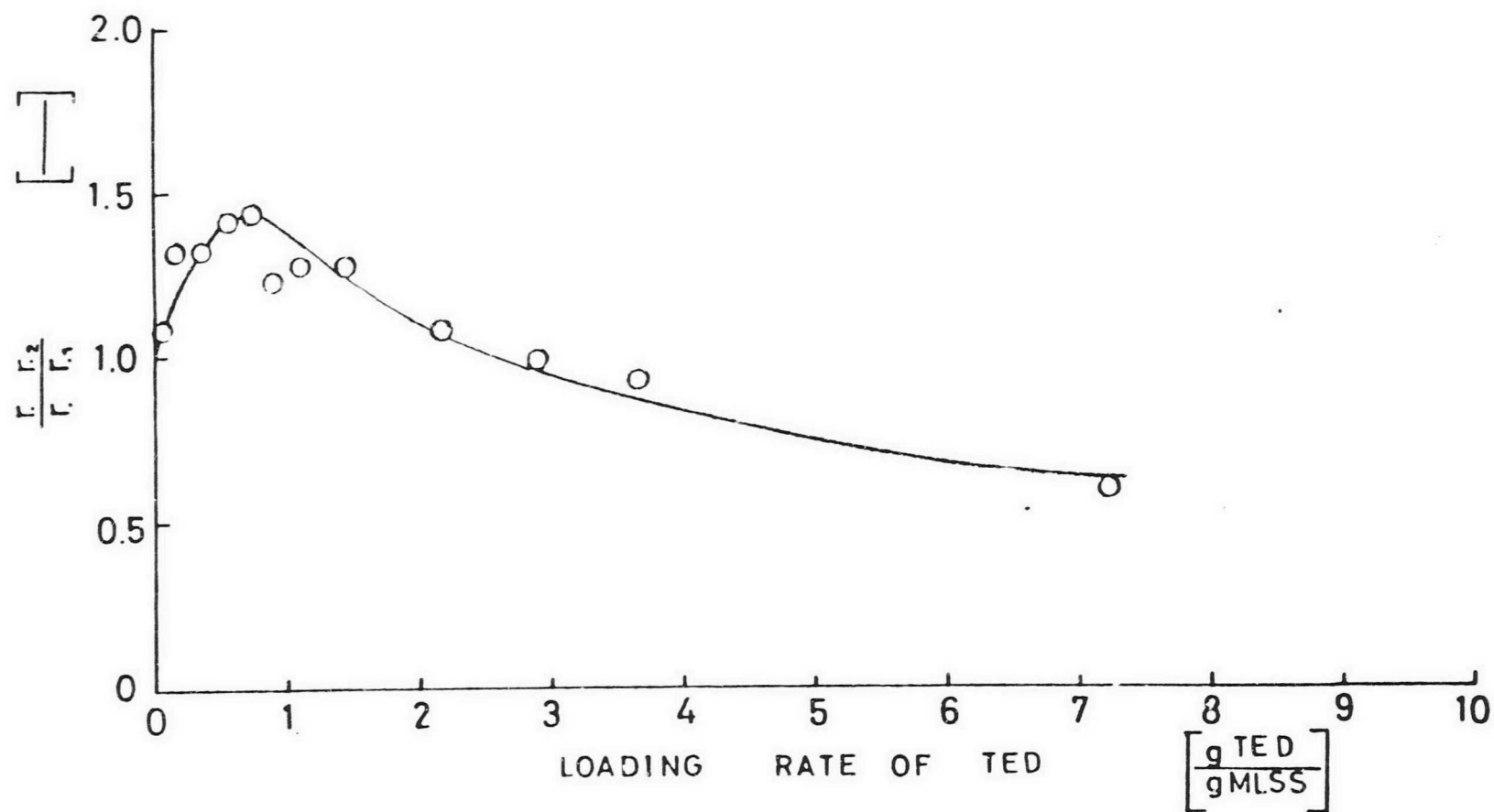
r. r.$_2$ ⋯⋯ respiration rate after loading

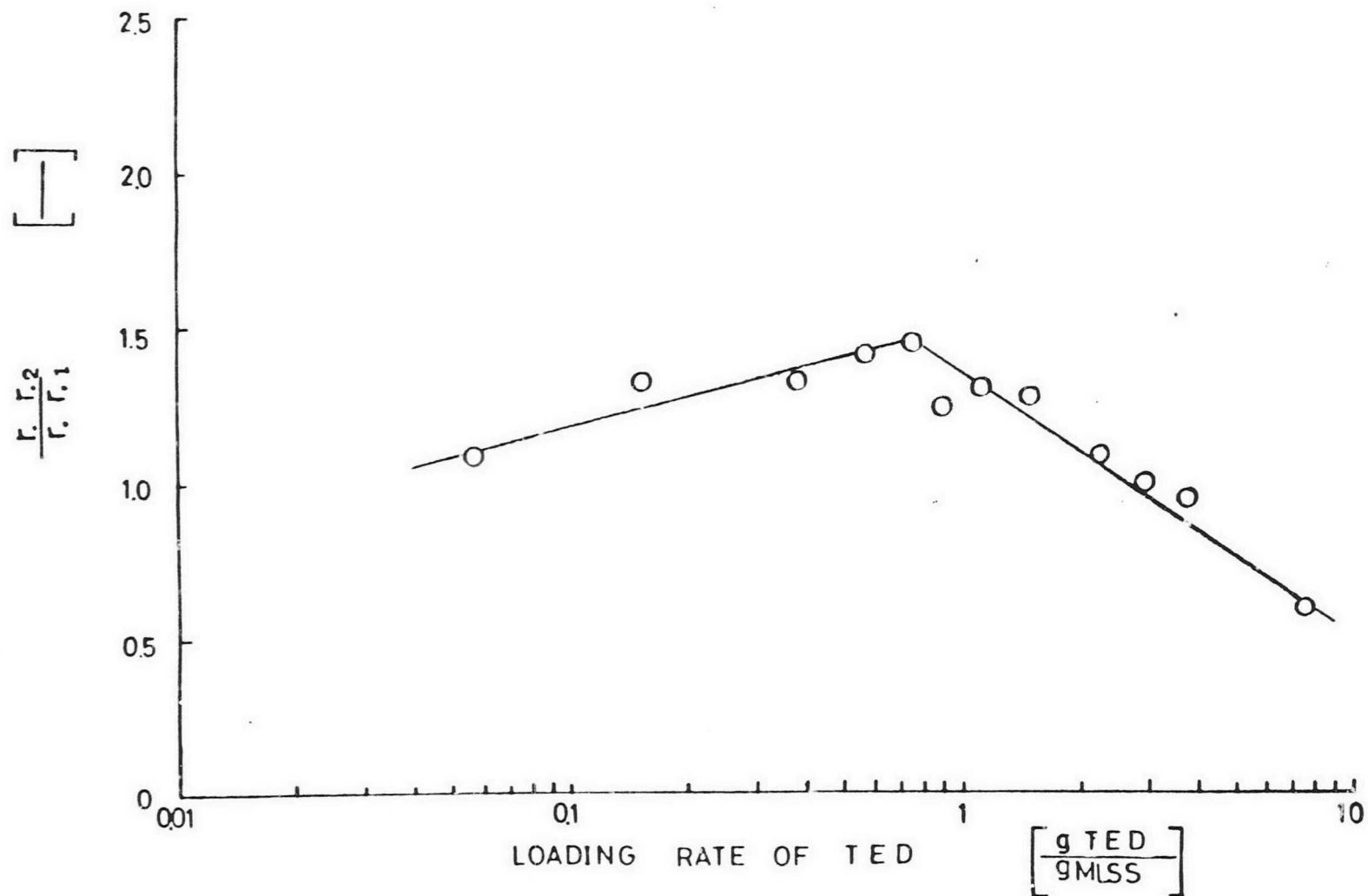Fig. 6S3-1   EFFECT OF TED ON ACTIVATED SLUDGE
(CONTINUOUS FEEDING)

Fig. 6 S 3-2 EFFECT OF TED ON ACTIVATED SLUDGE
(CONTINUOUS FEEDING)

DATE 12/8

AERATION TANK No.	IV	LOADING CONDITION	Over loading
TEMPERATURE (°C) T		pH	6.42
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO	0.8	OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1535	INFLUENT COD(mg/l) COD_{in}	79.0
SPECIFIC VOLUME SV_{30}	18.0	EFFLUENT COD (mg/l) COD_{eff}	32.3
SLUDGE VOLUME INDEX (ml/gMLSS) SVI	117	REMOVAL EFFICIENCY OF COD (%)	59
INFLUENT WATER FLOW RATE (l/day)	194	FOOD:MICROORGANISM RATIO F/M (gCOD/gMLSS·day)	0.102
HYDRAULIC DETENTION TIME (hr^{-1})	12.1	RESPIRATION RATE (mg O_2/hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella]:[Rotifera] = 2:1
Hyphomycetes were found.

TABLE 6S4-1

Effect of TED solution on respiration rate of activated sludge system (EXCESS SUBSTRATE LOADING)

TED ppm	Loading rate g.TED/gMLSS	$r.r_1$ $\frac{mgO_2}{hr\ gMLSS}$	$r.r_2$ $\frac{mgO_2}{hr\ gMLSS}$	$\frac{r.r_1}{r.r_2}$
3790	2.17	25.4	28.1	1.11
1520	0.990	30.5	26.2	1.22
7560	4.93	23.6	19.5	0.82
4550	2.96	23.8	21.9	0.92
760	0.445	21.5	28.9	1.35
2260	1.49	20.7	23.8	1.15
5050	3.95	21.4	16.8	0.79
630	0.248	18.0	23.8	1.32
3040	1.96	23.8	27.4	1.15
1140	0.743	18.4	34.2	1.32

$r.r_1$ .... respiration rate before loading

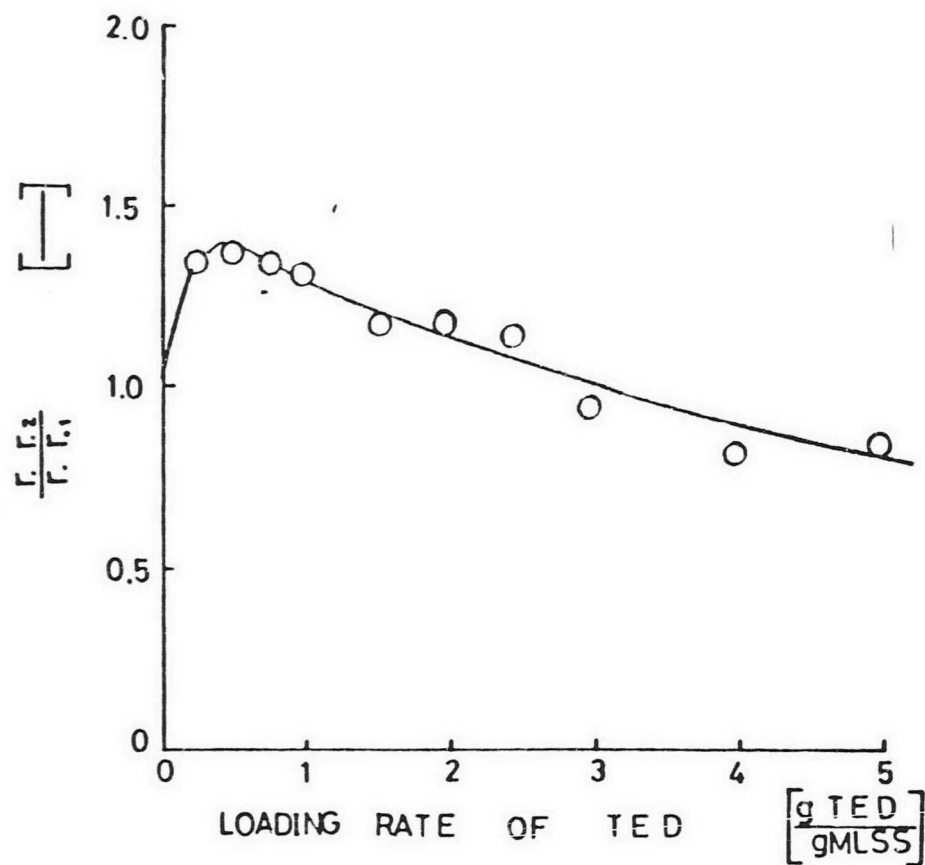$r.r_2$ .... respiration rate after loading

Fig. 6S4-1   EFFECT OF TED   ON ACTIVATED   SLUDGE
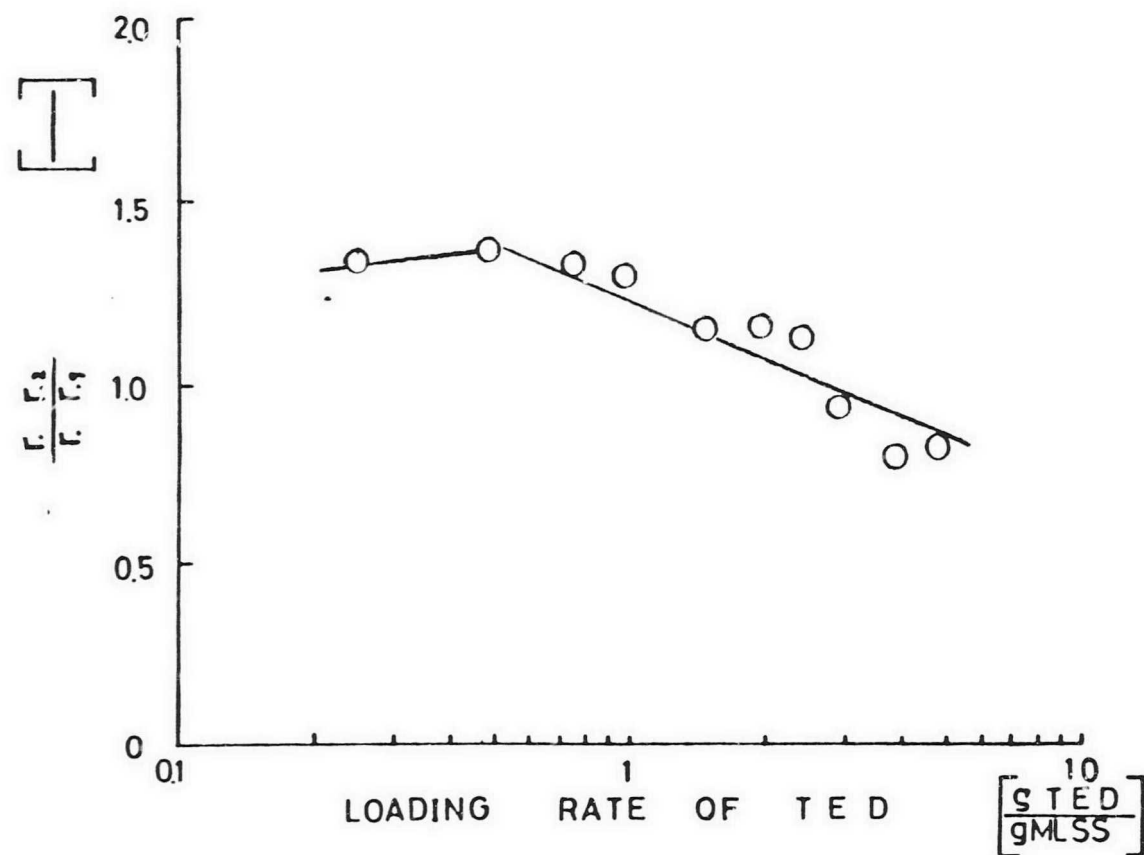WITH   EXCESS   SUBSTRATE   LOADING

Fig. 6S4-2 EFFECT OF TED ON ACTIVATED
SLUDGE WITH EXCESS SUBSTRATE LOADING

DATE 12/9

6S5-0

AERATION TANK No.	I	LOADING CONDITION	Without feeding
TEMPERATURE (°C) T		pH	5.98
DISSOLVED OXYGEN CON-CENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	656	INFLUENT COD(mg/l) COD_{in}	___
SPECIFIC VOLUME SV_{30}	3.0	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	45.7	REMOVAL EFFICIENCY OF COD (%)	___
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	___
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr · gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

Vorticella was not found.
[Rotifera] = 1
Hyphomycetes were found.

TABLE GS5-1

Effect of TED solution on respiration rate of activated sludge system (endgenous)

TED ppm	Loading rate gTED/gMLSS	$r.r_1$ $\frac{mgO_2}{hr\,gMLSS}$	$r.r_2$ $\frac{mgO_2}{hr\,gMLSS}$	$\frac{r.r_1}{r.r_2}$
2120	3.23	7.32	10.7	1.46
4240	6.45	6.46	6.40	1.00
850	1.30	7.62	10.7	1.40
1280	1.95	7.93	10.1	1.27
2550	3.89	6.10	6.10	1.00
430	0.655	4.57	10.7	2.33
1700	2.59	5.49	7.93	1.44
3390	5.17	4.88	4.88	1.00
210	0.320	4.88	7.62	1.56
640	0.973	3.96	3.96	1.00

$r.r_1$ ...... respiration rate before loading

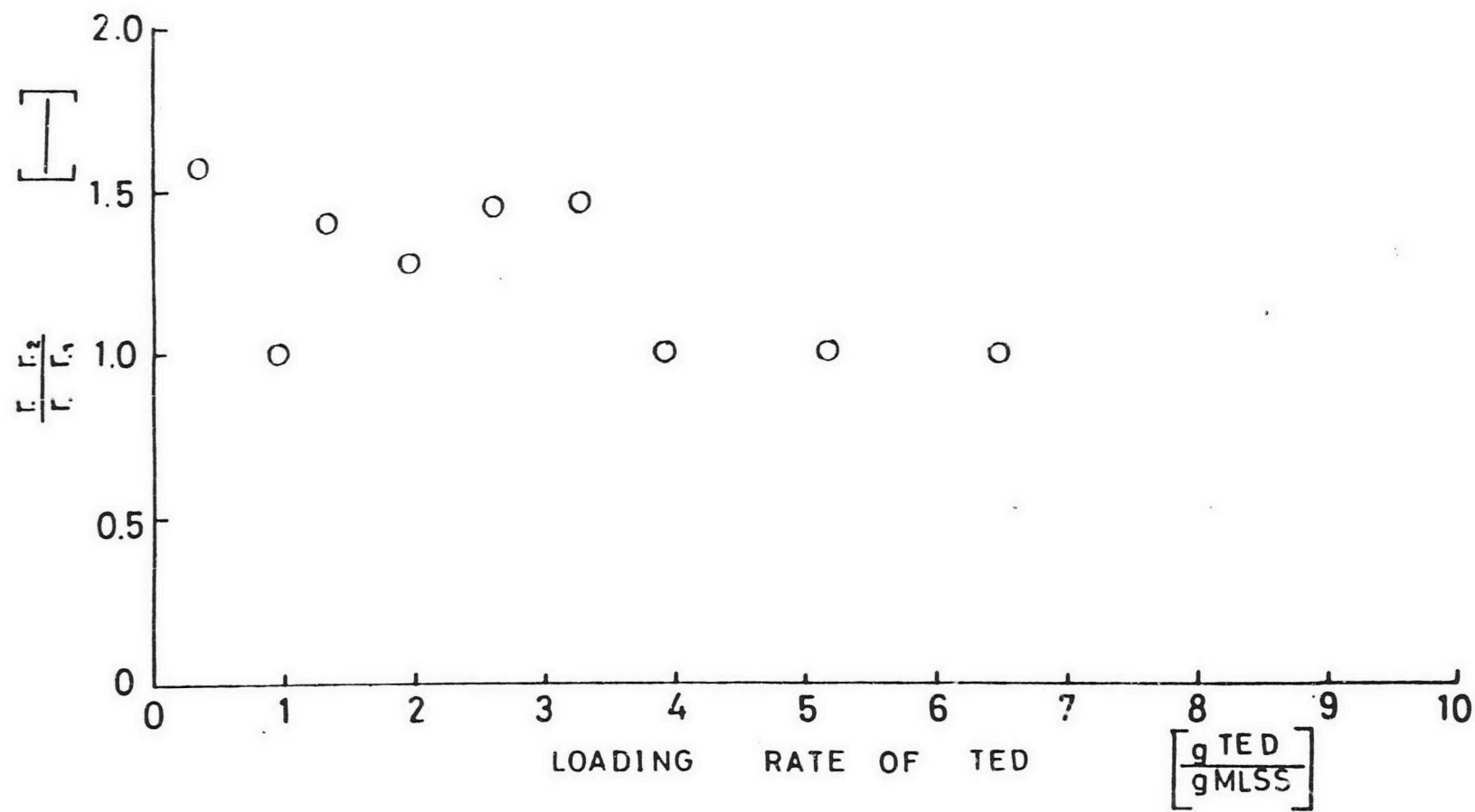$r.r_2$ ...... respiration rate after loading
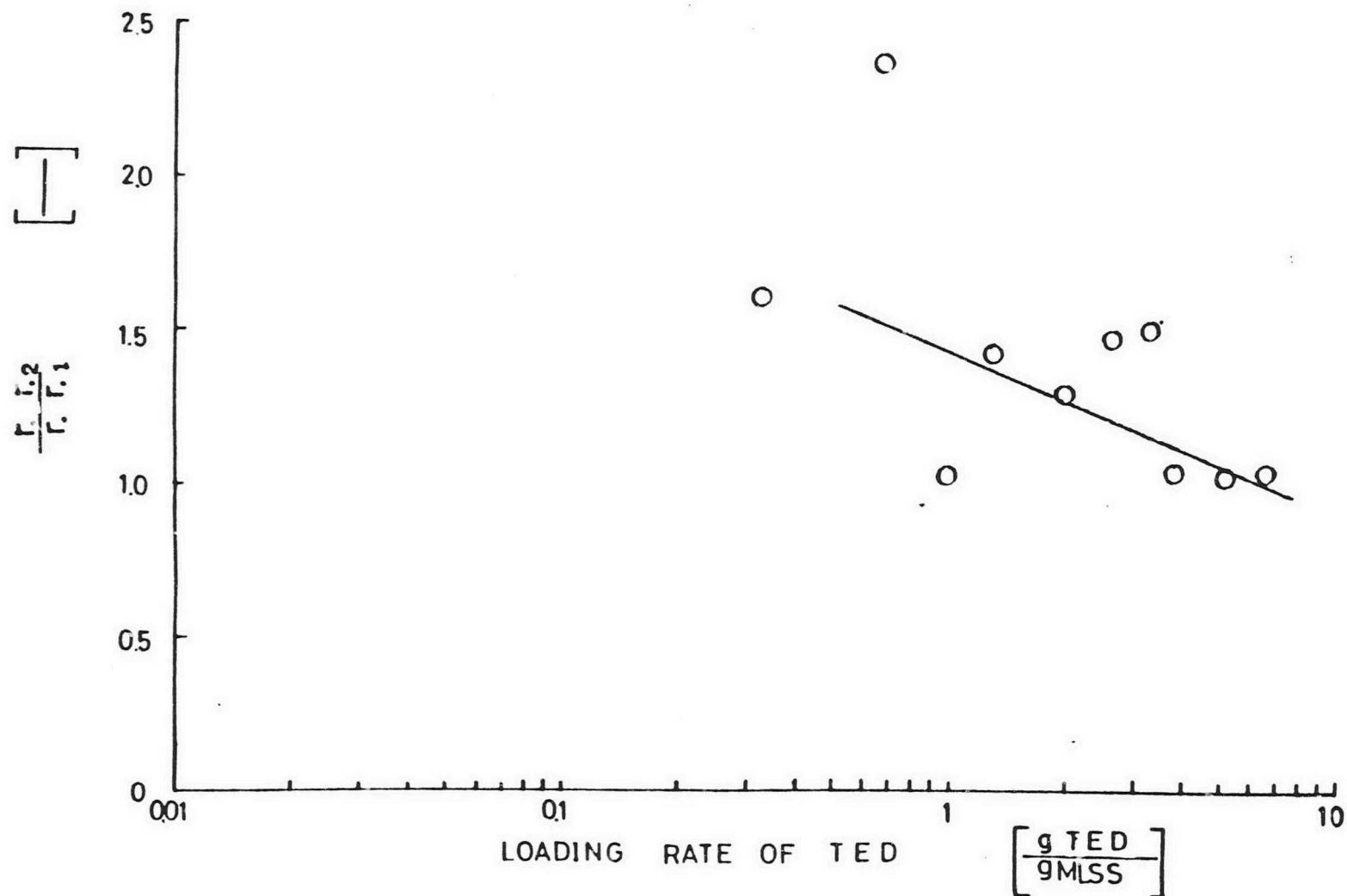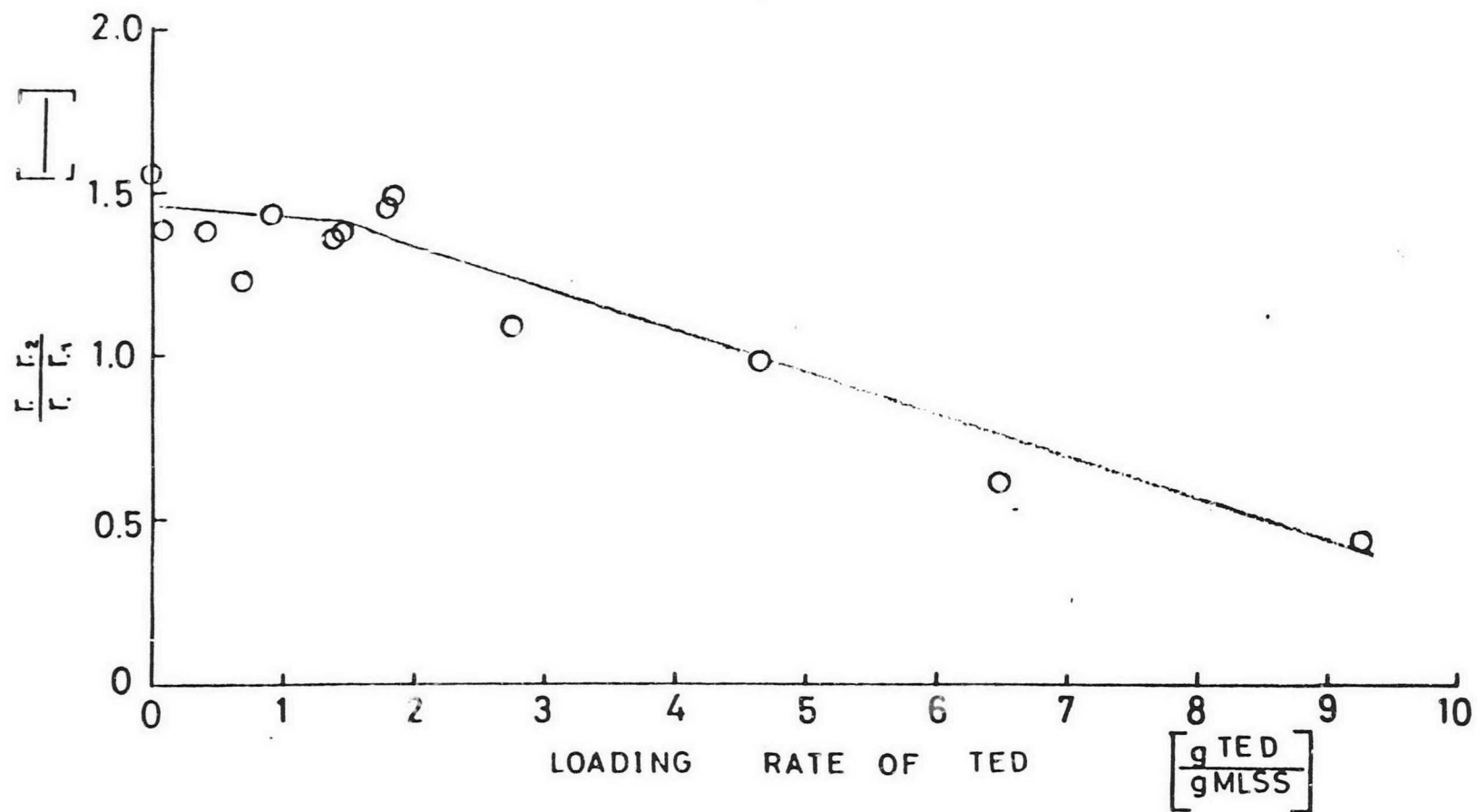
Fig 6S5-1   EFFECT OF TED ON ACTIVATED SLUDGE (endogenous)

Fig. 6S5-2 EFFECT OF TED ON ACTIVATED SLUDGE (endgenous)

DATE 12/14

6S6-0

AERATION TANK No.	IV	LOADING CONDITION	Without feeding
TEMPERATURE (°C) T	17	pH	6.80
DISSOLVED OXYGEN CONCENTRATION (mg/l) DO		OXIDATION – REDUCTION POTENTIAL (mV) ORP	
MIXED LIQUOR SUSPENDED SOLID CONCENTRATION (mg/l) MLSS	1267	INFLUENT COD (mg/l) COD_{in}	——
SPECIFIC VOLUME SV_{30}	58	EFFLUENT COD (mg/l) COD_{eff}	
SLUDGE VOLUME INDEX (ml / gMLSS) SVI	453	REMOVAL EFFICIENCY OF COD (%)	——
INFLUENT WATER FLOW RATE (l /day)		FOOD : MICROORGANISM RATIO F / M (gCOD / gMLSS·day)	——
HYDRAULIC DETENTION TIME (hr^{-1})		RESPIRATION RATE (mg O_2 / hr·gMLSS)	

MICROSCOPIC OBSERVATION & COMMENT

[Vorticella] : [Rotifera] = 4 : 2

Vorticella and Rotifera were not active.

Hyphomycetes were found.

TABLE 656-1

Effect of TED solution on respiration rate of activated sludge system (endgenous)

TED ppm	Loading rate g.TED /gMLSS	r. r.$_1$ mgO$_2$ / hr gMLSS	r. r.$_2$ mgO$_2$ / hr gMLSS	r. r.$_1$ / r. r.$_2$
2370	1.87	5.45	8.05	1.48
1906	1.50	6.39	8.75	1.37
2370	1.87	7.81	11.4	1.45
5900	4.66	6.63	6.39	0.96
1190	0.939	6.59	9.39	1.43
11700	9.23	9.47	4.03	0.43
590	0.466	9.00	12.3	1.37
3550	2.80	6.63	7.10	1.07
8240	6.50	7.81	4.74	0.61
120	0.0947	6.63	9.23	1.39
24	0.0189	4.97	7.81	1.57
1780	1.40	6.63	9.00	1.36
890	0.702	8.05	9.71	1.21

r. r.$_1$ .... respiration rate before loading

r. r.$_2$ .... respiration rate after loading

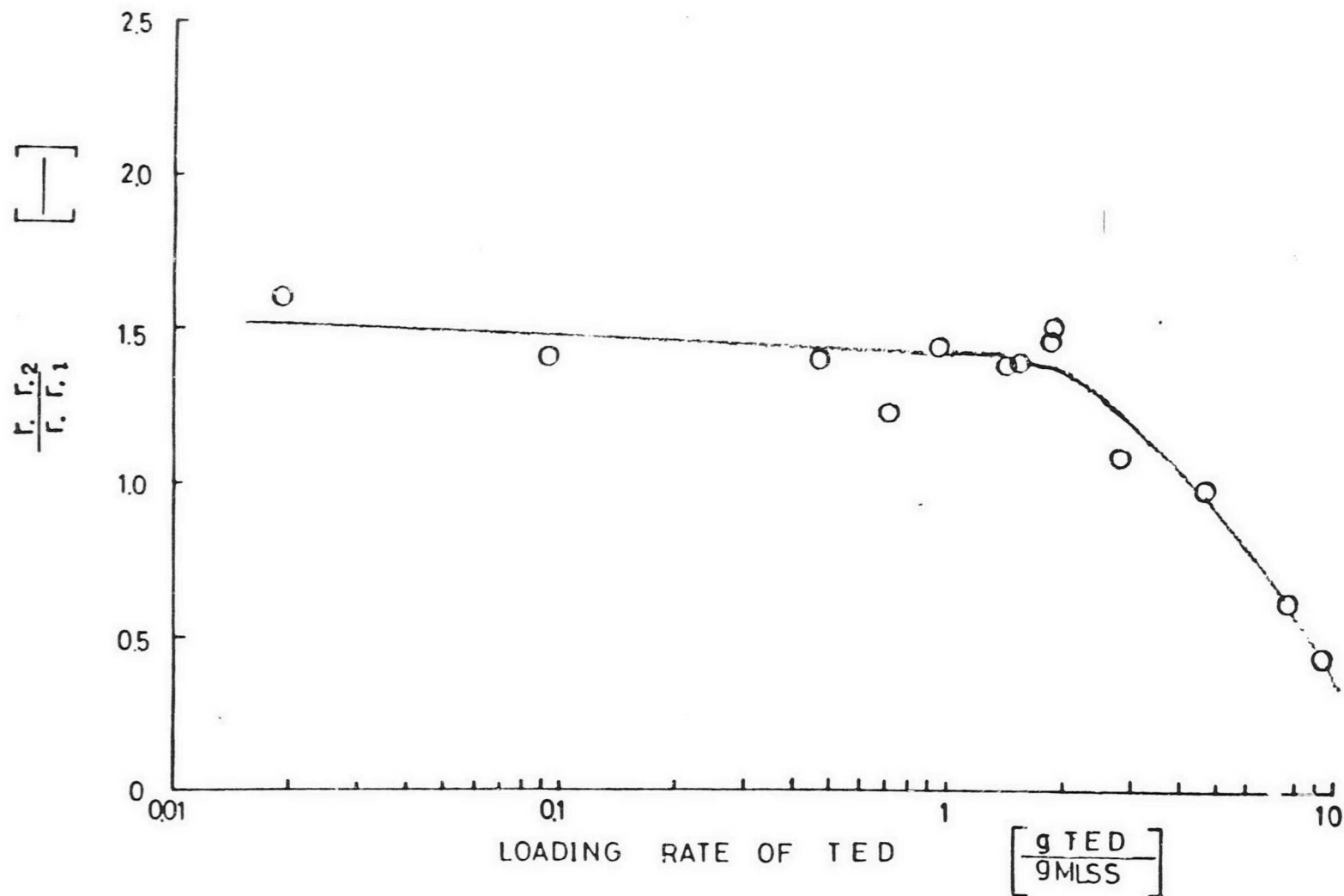Fig. 6 S6-1   EFFECT OF TED ON ACTIVATED SLUDGE (endogenous)

Fig. 6S6-2 EFFECT OF TED ON ACTIVATED SLUDGE (endogenous)

7. Appendix

Monitoring instrumentations

In this system, the following informations were recorded.
(a) temperature (b) pH (c) dissolved oxygen (d) oxidation
reduction potential.

The interface between instruments is important to obtain the
correct signals because the sensors associated with the above
parameters were not always insulated each other. The block
diagram of measureing system is shown in Fig.A-1, where the
recorder interference insulates the instruments each other
and transfers the information to recorder at the same time.
The circuit diagram of each insulating amplifier is given
in Fig.A-2. The insulation between instruments was about
10 $M\Omega$. However, this value is not sufficient for separation
of pH meter and ORP measuring instruments. Thus, the
differential type amplifier with the imput impedence of
$10^{12}\ \Omega$ was used for ORP measurement. The circuit diagram
is shown in Fig.4-3.

To supply a stable electric voltage to each instrument, the
stabilized power supply such as Fig.4-4 was used.
The stability of the power supply against output current and
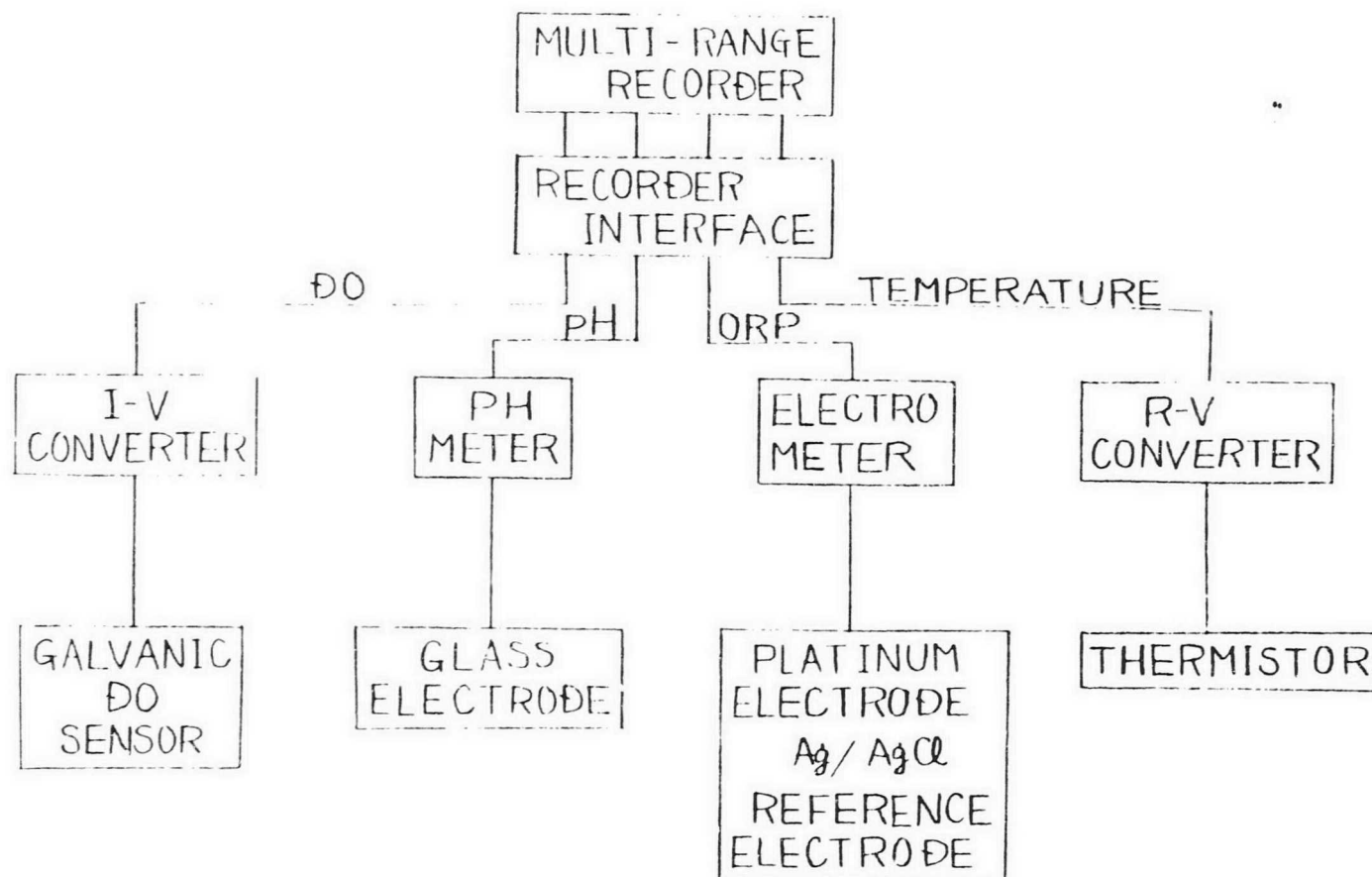a.c. line disterbunce are given in Fig.4-5 and 4-6.
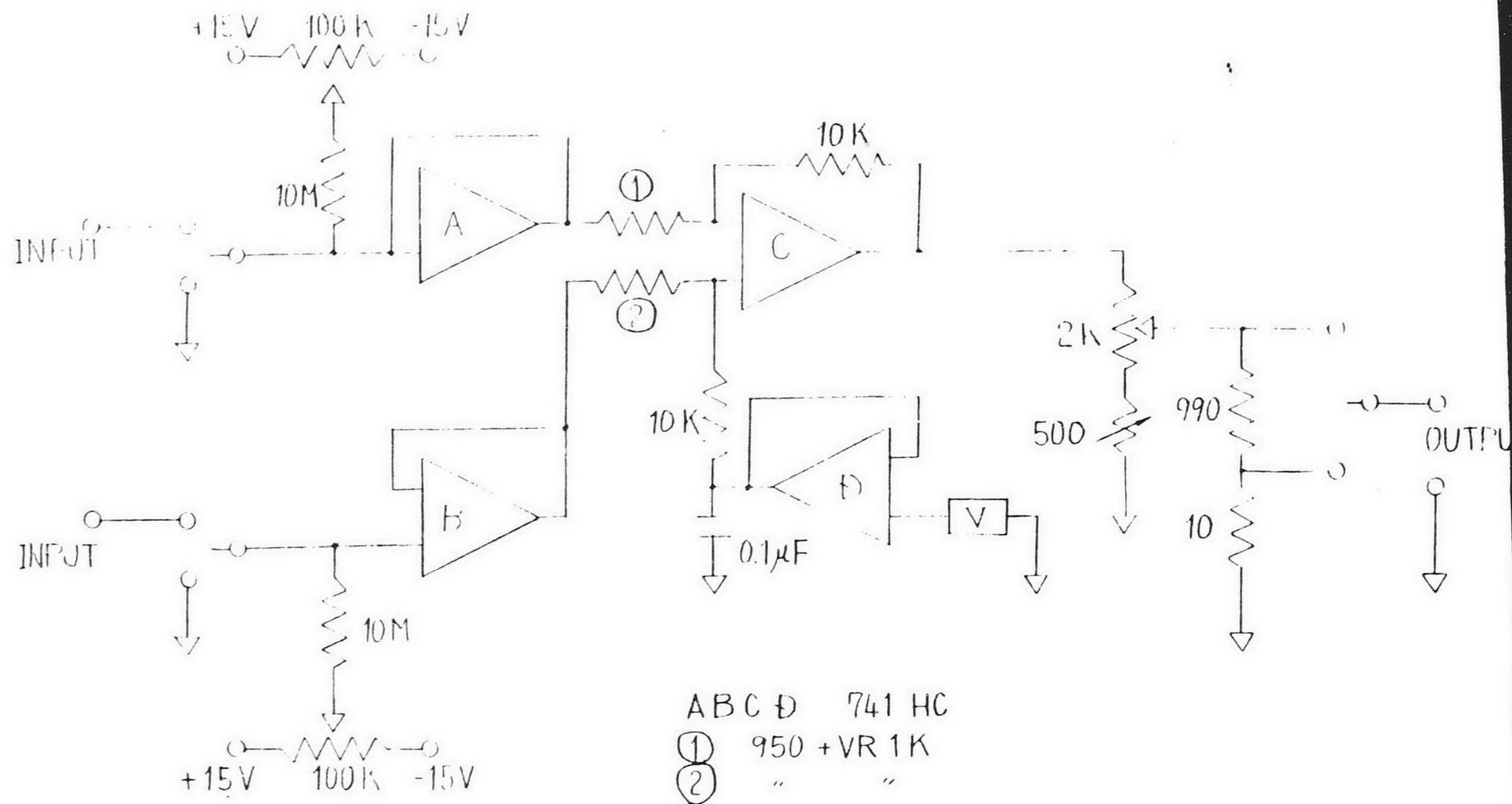
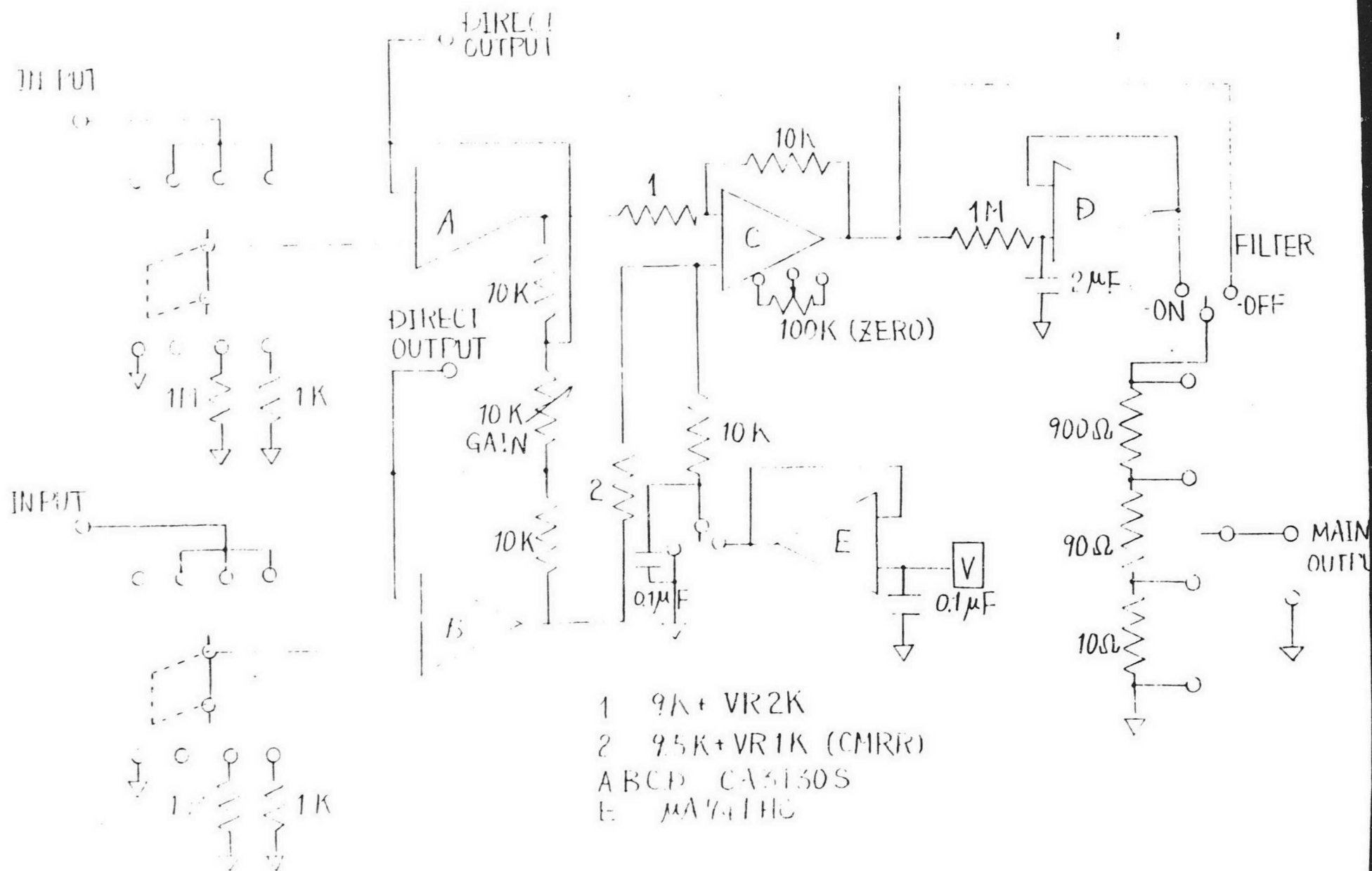Fig. A-1 Monitoring system

Fig A-2. Recorder interface
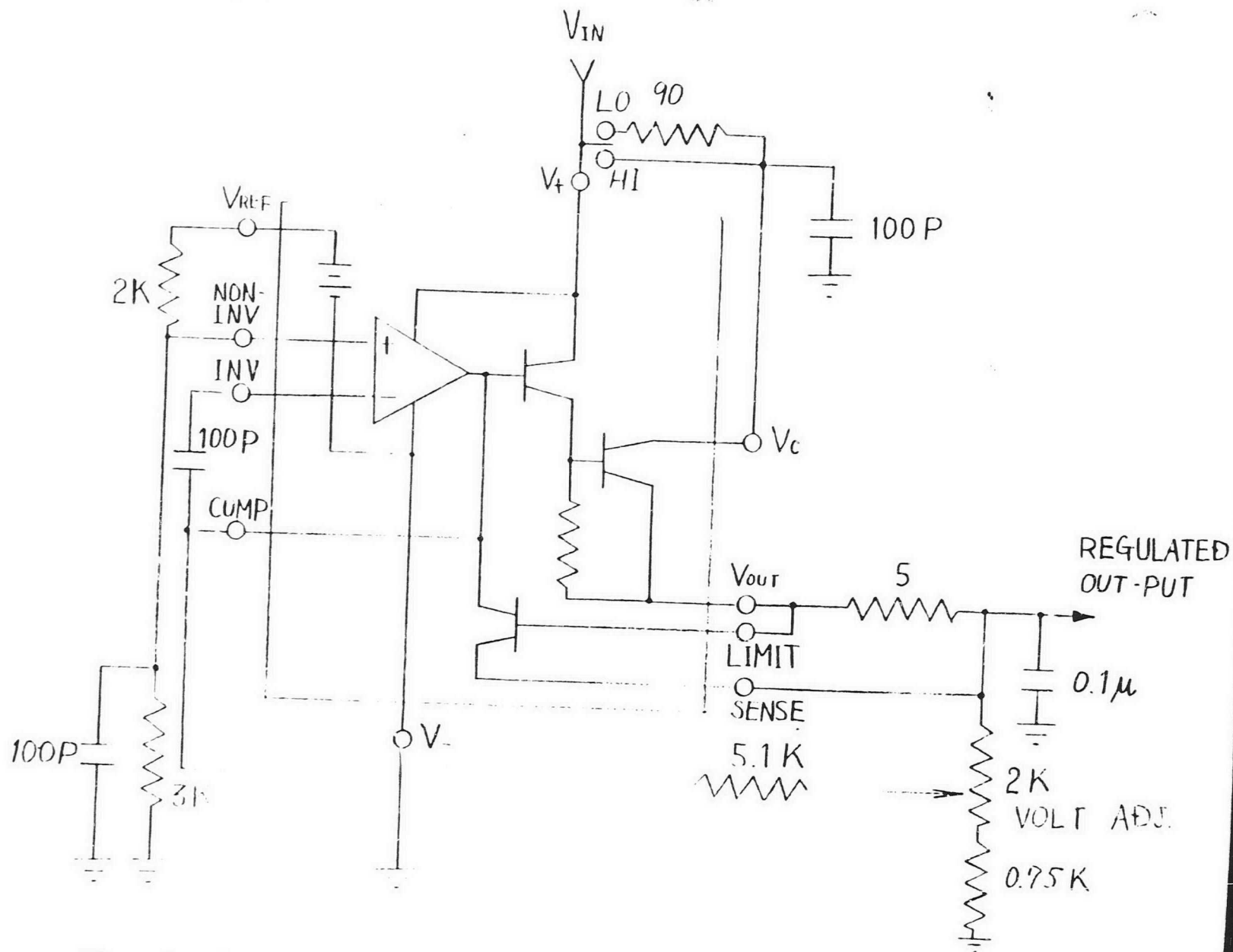
Fig. A-3   Electrometer
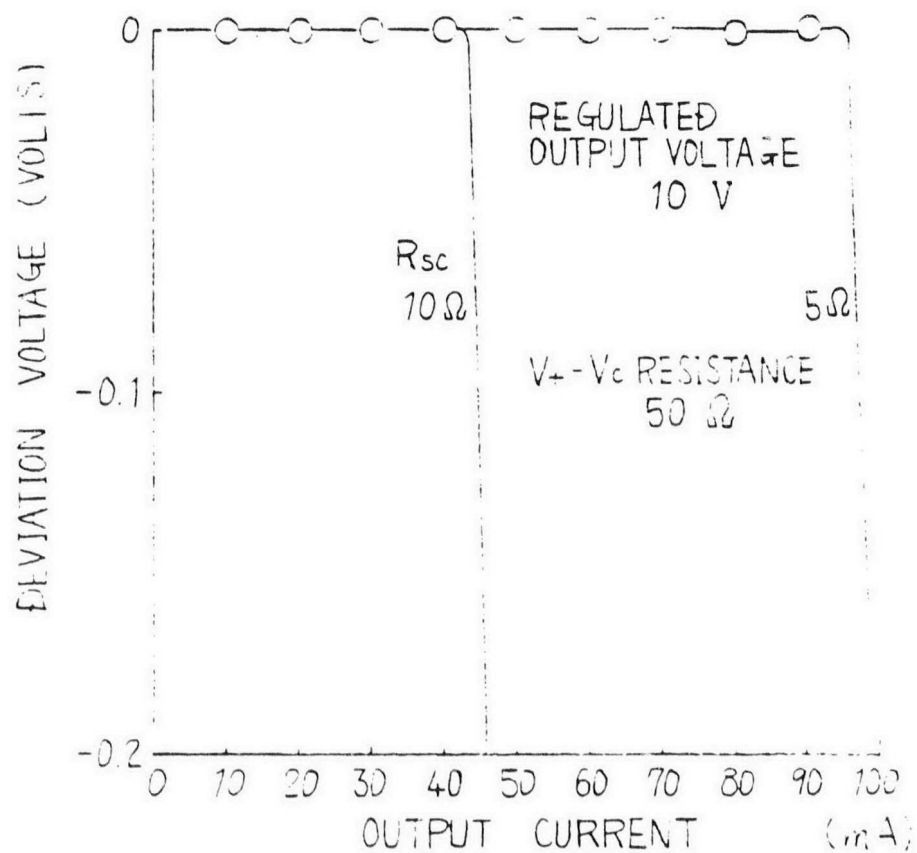
Fig. A-4 Voltage regulators (Type 723. 1C)

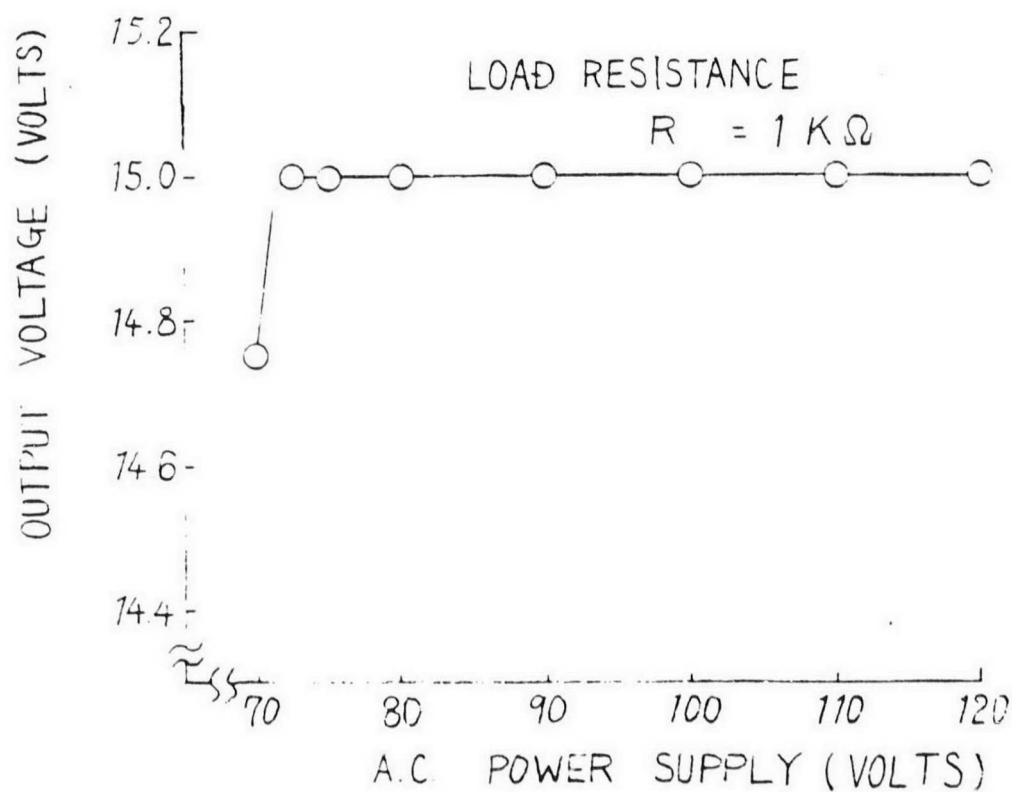Fig. A-5 Stability of power supply
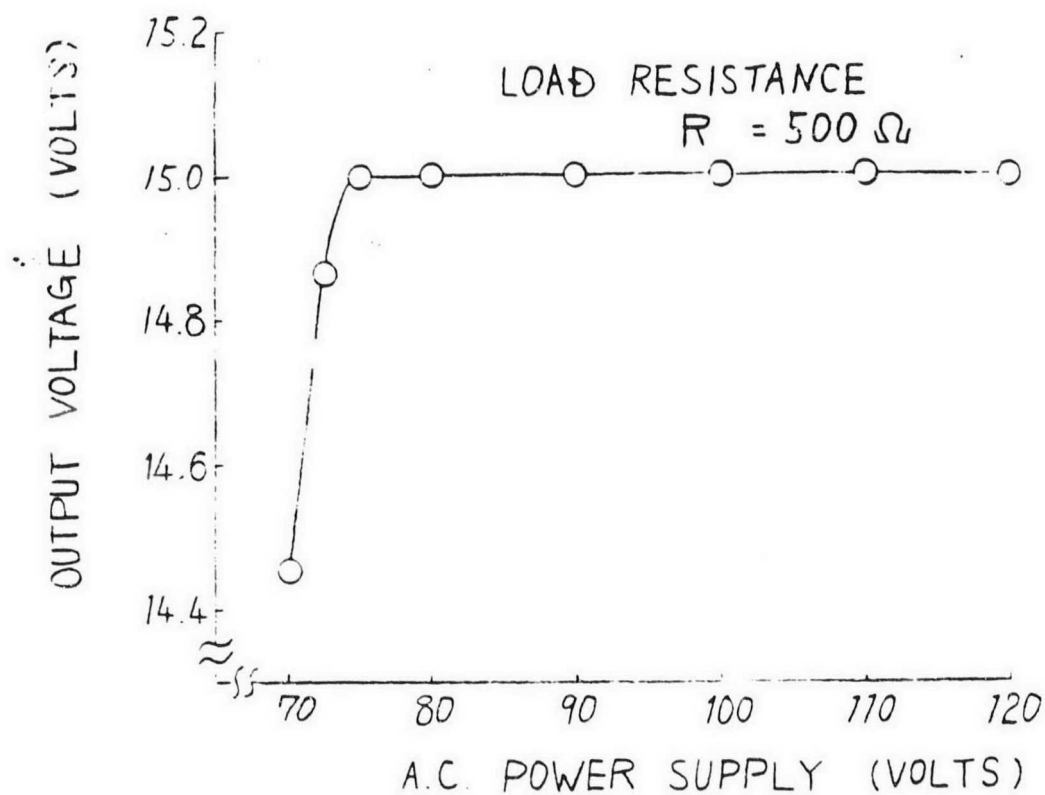with respect to the
output current

Fig. A-6   Stability of power supply with respect to the A.C. source perterbation

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